Pergamon

Tetrahedron, Vol. 53, No. 45, pp. 15515-15534, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00977-0

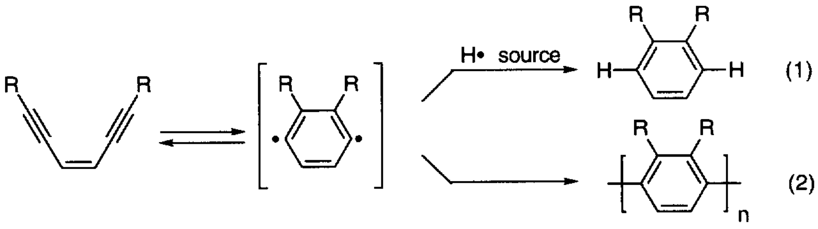
Synthesis of Polyphenylene Derivatives by Thermolysis of Enediynes and Dialkynylaromatic Monomers

Jens A. John and James M. Tour*

Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208

Abstract: Described are the syntheses of substituted enediynes and dialkynylaromatics using Pd- or Pd/Cu-catalyzed cross coupling procedures. The products were then thermalized to afford the corresponding poly(*p*-phenylene)s, poly(1,4-naphthalene)s, poly(benzo[*c*]thiophene)s, and poly(dibenzothiophene)s. Fifteen examples are provided that show the scope of the polymerization process based upon substituent patterns and cyclization moieties. The superb thermal resiliency of the newly derived polymers is demonstrated using thermogravimetric analysis. The polymer structure was generally confirmed using IR data correlations to small molecules that resembled the polymers' repeat unit structure. Radical trapping of dimeric intermediates, that were analyzed by GCMS, further substantiated the proposed mechanistic route. The step-growth polymerization pattern was determined by monitoring the degree of monomer consumption versus the polymer molecular weight. © 1997 Elsevier Science Ltd.

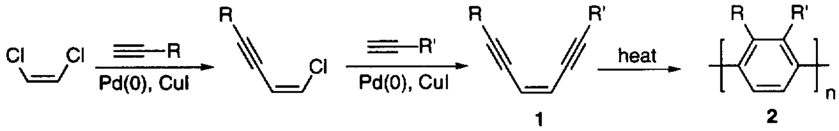
Bergman's study on the thermal cycloaromatization of enediynes led to the suggestion of a benzene 1,4-diradical intermediate.[1] Numerous synthetic and mechanistic studies were later performed to further investigate this reaction and a variety of enediynes have been thermalized in the presence of radical terminators such as 1,4-cyclohexadiene (eq 1).[1,2] Even though large excesses of radical terminators were employed, the yield of the substituted benzenes were often moderate at best. The fact that the yields were diminutive kindled our interest because it suggested to us that polymerization may indeed be a preferred pathway and we could regard the intermediate benzene 1,4-diradical as a building block for substituted polyphenylenes. As suspected, deletion of the radical trapping source from the reaction mixtures allowed for the formation of substituted polyphenylenes (eq 2).[3]



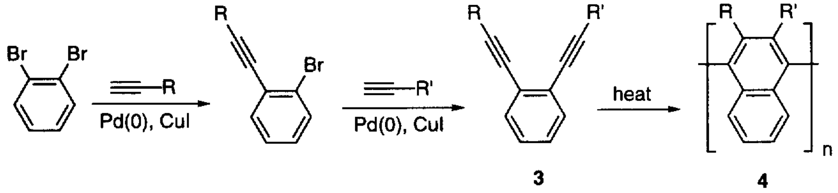
Substituted polyphenylenes have been shown to exhibit superb thermal and chemical resilience, interesting semiconducting properties upon doping, and applications in light emitting diodes.[4,5] Therefore, this route to polyphenylenes and their derivatives is most attractive since (1) it requires no exogenous chemical catalysts or reagents for the polymerization, (2) heteroatomic coupling sites such as halogens are not necessary,

(3) all atoms present in the monomer are also present in the polymer, (4) the monomers can be rapidly prepared with a variety of substitution patterns to often afford soluble polyphenylene derivatives, and (5) the process is amenable to a vapor deposition of polyphenylene flims.[3e]

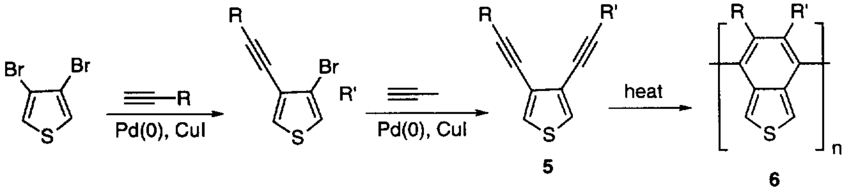
We could rapidly prepare numerous enediynes and dialkynylbenzenes by the Pd/Cu coupling protocol or an alkynylzinc chloride/Pd coupling.[6,7] Subsequent heating of the enediynes or dialkynylaromatics led to polymerization products (eqs 3-6). The results of the polymerization are summarized in Table 1. We found that highest molecular weights could be obtained using benzene as a solvent and heating the monomers in thick-walled screw cap glass tubes[8] at 50-160°C. In a few cases, when the polymerizations required higher temperatures, they were conducted on neat materials.



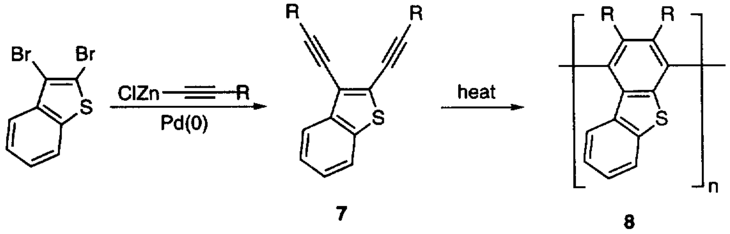
(3)



(4)



(5)



(6)

Table 1. Thermal Polymerization of Enediynes and Dialkynylarenes to Afford Polyaromatics.[a]

Entry	Monomer	R	R'	Temp[b]	M_w[c,d]	M_n[d,e]	solubility[f]	$T_{10\%}$[g,h]	$T_{50\%}$[h,i]	color[j]
1	1	H	*n*-C_6H_{13}	120	3930	1570	soluble	287	472	brown
2	1	H	Ph	150	305000[k]	9500	soluble	392	>900	tan
3	1	H	(*p*-C_6H_4)-Ph	95	10600	4100	soluble	438	>900	tan
4	1	H	(*o*-C_6H_4)-Ph	50-90	3200	2000	soluble	432	791	tan
5	1	H	(*p*-C_6H_4)-CMe_3	50-95	6500	2600	soluble	428	898	brown
6	1	H	(1-naphthyl)	115	5500	1450	soluble	416	>900	tan
7	1	H	(9-anthryl)	120	9400	800	partial soluble[l]	351	>900	orange[m]
8	1	*n*-C_6H_{13}	*n*-C_6H_{13}	140	980	810	soluble[n]	178	375	green
9	1	$SiMe_3$	$SiMe_3$	300[o]	2850	1040	soluble	248	490	black
10	3	H	H	140	---	---	insoluble	500	>900	brown
11	3	H	Ph	140	1200	850	soluble	380	617	tan
12	3	Ph	Ph	400[o]	---	---	insoluble	606	>900	black
13	3	*n*-C_6H_{13}	*n*-C_6H_{13}	340[o]	---	---	insoluble	507	>900	black
14	5	H	Ph	160	3470	1280	soluble	445	747	brown
15	7	H	---	150	---	---	insoluble	409	>900	brown

[a] Dashes signify that the value was not obtained or it was not clearly discernable during the analysis. Unless otherwise noted, all reactions were carried out in a thick-walled screw-capped tube in benzene (0.7-1.1 M) as the solvent. [b] Temperature in °C used for the polymerization. The reaction times were generally 24-48 h. [c] Weight average molecular weights. [d] Determined by size exclusion chromatography (SEC) in THF versus polystyrene standards. [e] Number average molecular weights. [f] Solubility in THF or CH_2Cl_2. [g] Temperature at which 10% weight loss occurred. [h] Determined by thermogravimetric analysis (TGA) from 50 to 900°C at 10°C/min under an N_2 atmosphere. [i] Temperature at which 50% weight loss occurred. [j] Color of neat polymer. [k] We presently have no explanation for the very broad polydispersity. [l] SEC data obtained on the soluble portion and TGA data obtained on the insoluble portion. [m] The monomer had an intense orange color. [n] Material was predominantly unreacted monomer. [o] The reaction was run without solvent.

In general, monomers that had both R and R' = H, afforded insoluble polymers. Monomers that had either R or R' = H, readily polymerized to afford soluble polymers. In the cases where neither R or R' = H, the polymerizations were often slower and they required higher temperatures and neat reaction conditions which likely caused polymer decomposition as flagged by the black color of the products (Table 1). The yields of the polymerized material were generally 50-90% after fractional precipitation. The obtained M_n values of 1500-2500 are quite typical for poly(*p*-phenylene) derivatives.[4] Note, however, that SEC-determined values of M_n versus polystyrene standards are inflated due to hydrodynamic volume differences of rigid rod polymers versus the randomly coiled polystyrene standards.

The superb thermal stabilities are apparent in that, in many cases, the unannealed polymers exhibited 10% weight loss only after exceeding 400-600°C (Table 1). Being unannealed, some of the early weight loss could be attributed to occluded solvent, therefore, these values represent a lower limit for thermal degradation.

The IR spectra are most informative in confirming the structure of the proposed polymers.[9] For the monosubstituted polyphenylenes (Table 1, entries 1-7), the polymer repeat unit possesses a 1,2,4-substituted phenyl pattern. The most diagnostic bands at 935-810 cm^{-1} are assigned to the bending of a lone hydrogen at the 3-position and the band at 880-795 cm^{-1} arises from the bending of two of the adjacent hydrogens at the 5- and 6-positions. Assignment of the disubstituted polyphenylenes can best be described using the bis(trimethylsilyl) derivative (Table 1, entry 9). The shoulder above 3000 cm^{-1} comes from the C-H stretching vibration. The band at 838 cm^{-1} results from out-of-plane C-H bending of two adjacent hydrogen atoms bound to a phenyl ring. Analysis of the 1,2-dialkynylbenzene-derived polymers argued in favor of the 1,4-disubstituted naphthalene structure (eq 4). For example, for the simplest case where R = R'= H (Table 1, entry 10), bands at 1595, 875 (two adjacent H) and 754 (four adjacent H) agreed with the literature values for 1,4-disubstituted naphthalenes.[9] For the heterocyclic polymers (eqs 5 and 6, Table 1 entries 14 and 15), again IR patterns suggested formation of the benzo[*c*]thiophene and dibenzothiophene moieties, respectively. For example, **6** exhibits bands at 3102, 3060, 1595, 1493, 1436, 1383, 1103, 1068, 877, 795, 754 and 692 cm^{-1}.[9c] The parent compound benzo[*c*]thiophene has diagnostic bands at 3110 and 875 cm^{-1} while the bands at 3060, 1595, 1493, 1436, 1068, 754 and 692 cm^{-1} are due to the phenyl substituent. Likewise **8** shows bands at 3055, 1580, 1435, 1312, 1159, 1130, 1065, 1021, 847, 759, 730, 679 and 650 cm^{-1}. The parent compound dibenzothiophene has bands at 3073, 1589, 1449, 1308, 1231, 1074, 1023, 739 and 619 cm^{-1}. The additional bands at 847, 759, 679 cm^{-1} are due to the 1,4-disubstitution pattern in the polymer.[9d]

The mechanistic aspects of the polymerization process are intriguing.[10] Two general mechanisms are considered. First, a benzene 1,4-diradical may be attacking unreacted enediyne to generate a new biphenyl 4,4'-diradical intermediate. Continued reaction of this growing chain with enediyne should result in a chain growth-like polymerization process in that the molecular weight of the polymer would increase rapidly even at low monomer conversions. Conversely, the benzene 1,4-diradical may predominantly couple with other radicals in solution to eventually form the polymer. In that case, the process should be step growth-like where the polymer molecular weight would initially increase slowly, but then increase rapidly when monomer conversion was nearly complete. By monitoring consumption of **1** (R = H, R' = Ph) (using capillary GC with terphenyl as an internal standard) and molecular weight (M_n and M_w by SEC), it was clear that the molecular weight increased slowly (M_n= 600 at 10% monomer consumption and 810 at 90% monomer consumption) until the monomer was nearly consumed (>97%), whereupon the molecular weight increased exceeding rapidly (Fig 1). Therefore,

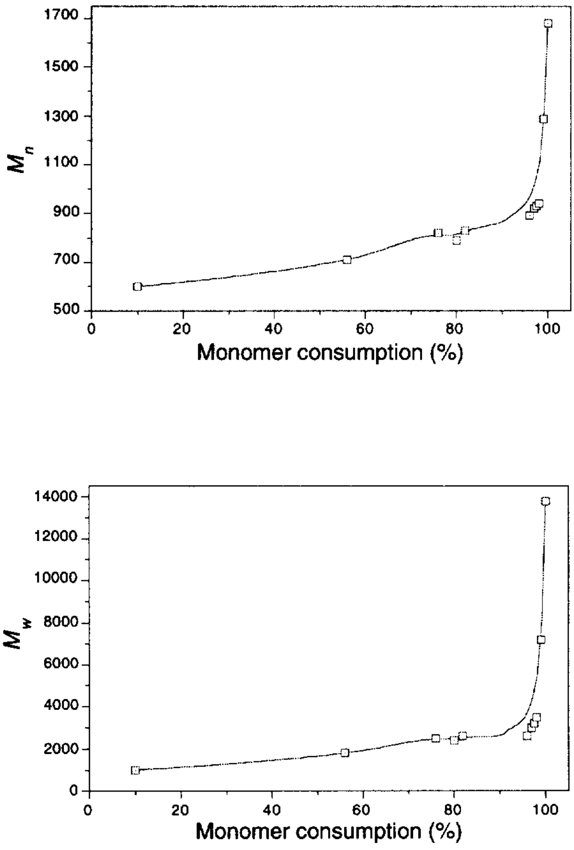


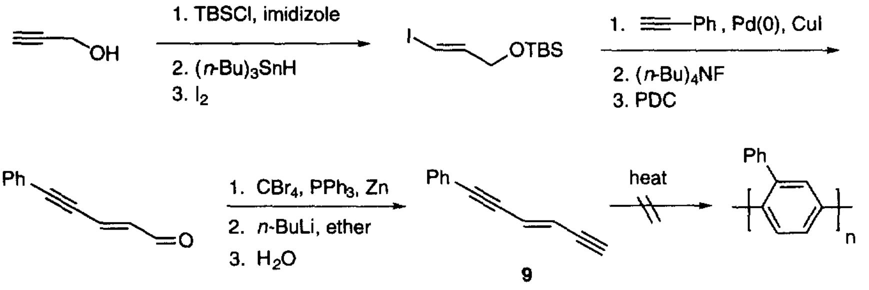
Figure 1. The number and weight average molecular weights of the polymer derived from **1** (R= H, R'= Ph) versus the percent of monomer consumption.

the polymerization indeed resembles a step growth process. Also, addition of small amounts of radical initiators did not increase the polymerization efficiency.

As a further conformation of the radical coupling process described here, we carried out the thermalization process for two of the monomers in the presence of the radical trapping agent 1,4-cyclohexadiene.

This was done with the hope of obtaining some small, characterizable dimeric species. Indeed, when **1** (R = H, R' = Ph) was heated in benzene in the presence 1,4-cyclohexadiene (33 mol %) at 150 °C, we observed the formation of polymeric material as well as several low molecular weight species detected by GC/MS analysis. The volatile material consisted of unreacted starting material, biphenyl (154 amu) and the desired dimeric adduct quaterphenyl (306 amu). Likewise, when **3** (R and R' = H) was heated in benzene in the presence 1,4-cyclohexadiene (21 mol %) at 150°C, polymer was formed as well as several volatile species. The volatile material consisted of unreacted starting material, naphthalene (128 amu), 1,4-cyclohexadienyl addition/aromatization products, and the desired dimer 1,1'-binaphthalene (254 amu). The isotopic pattern and fragmentation pattern matched identically with the mass spectral data base-derived 1,1'-binaphthalene spectrum.

Finally, it has been shown that *E*-enediynes do not undergo the Bergman cyclization.[1] We therefore prepared the *E*-enediyne **9** as shown in eq 7. Heating this monomer to 150 °C for 2 days did indeed form a



9

(7)

polymer, however, FTIR analysis verified that it was not a polyphenylene-derived material in that the two bands at 935-810 cm^{-1} and 880-795 cm^{-1} were missing.

In summary, we have outlined the scope of enediyne polymerizations to form poly(phenylene)s and their derivatives. This method is particularly well-suited for polymerizations since it requires no exogenous chemical catalysts or reagents for the process, and it is a non-condensation process wherein no volatile by-products are formed in the polymerization reaction. It is therefore amenable to a polymer film-forming vapor deposition process.[3e] Additionally, numerous different monomers can be rapidly synthesized using metal-catalyzed coupling reactions.

General Experimental Procedures. All synthetic operations were carried out under a dry, oxygen-free, nitrogen atmosphere. ^{1}NMR spectra were recorded at 300 or 500 MHz on Brüker AM-300 or Brüker AM-500 spectrometers, respectively. The ^{13}C NMR spectra at 75 or 125 MHz were recorded on Brüker AM-300, or Brüker AM-500 spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm down field from tetramethylsilane (TMS) and ^{13}C resonances (unless otherwise noted) were recorded using the 77.0-ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm down field from TMS. Infrared spectra were recorded on a Perkin Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical, Ltd., 70SQ high resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. Molecular weight analyses (SEC) were performed using two 30 x 75 cm Burdick and Jackson GPC columns (105 Å 10 μm and 500 Å 5 μm) eluted with THF at 60 °C (flow rate 1.0 mL/min, 700 psi), a Perkin

Elmer LC 250 pump, and a Perkin Elmer LC-30 RI detector. Molecular weight results were based on eight polystyrene standards (with a correlation coefficient >0.9998) purchased from Polymer Laboratories Ltd. Capillary GC analyses were obtained using a Hewlett Packard Model 5890 gas chromatograph using a Hewlett Packard 3396 A integrator. Alkyllithiums were purchased from Aldrich Chemical Company Inc. or Lithium Corporation of America. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade benzene and dichloromethane were distilled over calcium hydride. Bulk grade hexane was distilled prior to use. Gravity column chromatography, silica gel plugs, and flash chromatography were carried out using silica gel (230-400 mesh from EM Science). Thin layer chromatography was performed using glass plates pre-coated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science.

General Procedure for the Pd/Cu-catalyzed coupling of a terminal alkyne with an aryl or alkenyl halide.[6] The alkyne, the alkenyl halide, copper(I) iodide, triphenylphosphine, bis(dibenzylideneacetone)palladium(0), *n*-butylamine and benzene were stirred together at room temperature under nitrogen in a screw cap tube. After completion, the reaction mixture was poured into aqueous ammonium chloride and the organic phase was separated. Then the organic phase was washed twice with aqueous ammonium chloride. The combined aqueous layers were once extracted with ether. After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. Column chromatography (silica gel, hexane) was used to purify the final products.

General Procedure for the Pd-catalyzed coupling of a terminal alkynylzinc chlorides with an aryl or alkenyl halide.[7] The alkyne and ether were cooled to -78 °C. *n*-Butyllithium was added and the reaction was stirred for 1 h. In the meantime, zinc(II) chloride was flame-dried under vacuum. After cooling to room temperature, THF and the lithium alkynylide were added to the zinc chloride. The reaction mixture was stirred at room temperature for 1 h. The aryl halide, triphenylphosphine, THF and bis(dibenzylideneacetone)palladium(0) were combined and the zinc reagent was added. The reaction was heated to 75 °C overnight. After completion, the reaction mixture was poured into aqueous ammonium chloride and the organic phase was separated. Then the organic phase was twice washed with aqueous ammonium chloride and once with water. The combined aqueous layers were once extracted with ether. After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane).

General Procedure for the desilylation of trimethylsilylalkynes. The trimethylsilylalkyne, ether, methanol, and potassium carbonate were stirred together at room temperature. After completion, the reaction mixture was poured into water and the organic phase was separated. Then the organic phase was washed twice with water. The combined aqueous layers were once extracted with ether. After drying the combined organic layers over magnesium sulfate, the solvent was removed *in vacuo*. The crude product was purified by column chromatography (silica gel, hexane).

2-Iodobiphenyl. 2'-Aminobiphenyl (1.70 g, 0.010 mol), water (10 mL) and concentrated hydrochloric acid (5 mL) were cooled to 0 °C. A solution of sodium nitrite (0.70 g, 0.010 mole) in water (10 mL) was added and the reaction was stirred for 30 min. A solution of potassium iodide (2.18 g, 0.013 mol) in water (100 mL) was added and the mixture was allowed to warm to room temperature overnight. After completion, the reaction mixture was poured into water and the organic phase was separated. Then the aqueous phase was extracted three times with ether. The combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuo to obtain 2.80 g (100%) of the title compound as a red oil. IR (neat) 3056.4, 2974.4, 1575.9, 1555.4, 1493.9, 1478.5, 1458.0, 1442.6, 1422.1, 1293.9, 1252.9, 1155.4, 1114.4, 1068.2, 1017.0, 1001.6, 945.2, 909.3, 765.7, 745.2, 699.0, 647.7, 606.7. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.9, 1.2 Hz, 1 H), 7.55 - 7.27 (m, 7 H), 7.02 (td, J = 7.9, 1.9 Hz, 1 H).

1-Phenyl-2-(2'-(trimethylsilyl)ethynyl)benzene. 2-Iodobiphenyl (2.8 g, 0.010 mol) was coupled with trimethylsilylacetylene (2.00 mL, 0.014 mol) as described in the Pd/Cu-catalyzed coupling procedure above using benzene (4 mL), copper(I) iodide (0.11 g, 0.579 mmol), triphenylphosphine (0.20 g, 0.763 mmol), *n*-butylamine (2.80 mL), bis(dibenzylideneacetone)palladium (0.22 g, 0.383 mmol) and benzene (6 mL) for 2 day to afford 1.71 g (64%) of the title compound as a yellow oil. IR (neat) 3056.4, 3025.6, 2953.8, 2892.3, 2153.8, 1471.8, 1430.8, 1251.3, 1209.8, 1106.3, 1075.2, 1044.1, 1007.8, 945.7, 862.8, 842.1, 759.2, 733.3, 697.1, 645.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (br t, J = 8.0 Hz, 3 H), 7.36 (m, 5 H), 7.26 (m, 1 H), 0.12 (s, 9 H).

1-Phenyl-4-(2'-(trimethylsilyl)ethynyl)benzene. 4'-Bromobiphenyl (2.33 g, 9.99 mmol) and trimethylsilylacetylene (1.70 mL, 0.012 mol) were coupled as described in the Pd-catalyzed coupling procedure above using ether (8.0 mL), *n*-butyllithium (8.0 mL, 1.6 M in hexane, 0.0128 mol), zinc(II) chloride (2.31 g, 0.0169 mol), THF (10 mL), triphenylphosphine (0.17 g, 0.648 mol) and bis(dibenzylideneacetone)palladium(0) (0.11 g, 0.19 mmol) overnight to yield 2.35 g (94%) of the title compound as a white solid. IR (KBr) 3035.9, 2964.1, 2902.6, 2164.1, 1476.9, 1405.1, 1251.3, 1115.7, 1006.0, 870.0, 840.2, 762.6, 720.0, 688.2, 639.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.7 Hz, 2 H), 7.56 (s, 4 H), 7.45 (app t, J = 7.7 Hz, 2 H), 7.35 (d, J = 7.2 Hz, 1 H), 0.31 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.14, 140.26, 132.37, 128.81, 127.61, 126.98, 126.83, 122.01, 105.02, 94.81, 0.00.

1-(1'-Naphthyl)-2-trimethylsilylethyne. 1-Bromonaphthalene (1.40 mL, 0.0101 mole) and trimethylsilylacetylene (1.70 mL, 0.012 mol) were coupled as described in the Pd-catalyzed coupling procedure above using ether (8.0 mL), *n*-butyllithium (8.0 mL, 1.6 M in hexane, 0.0128 mol), zinc(II) chloride (2.24 g, 0.016 mol), THF (10 mL), triphenylphosphine (0.15 g, 0.572 mol), bis(dibenzylideneacetone)palladium(0) (0.11 g, 0.19 mmol) and THF (10 mL) overnight to yield 1.80 g (79%) of the title compound as a yellow oil after distillation (225°C, 4 mm Hg). IR (neat) 3058.8, 2958.9, 2898.4, 2146.6, 1586.1, 1508.3, 1392.8, 1270.5, 1249.7, 1075.5, 1040.3, 1012.7, 882.1, 842.8, 798.9, 772.8, 759.6, 730.6, 698.9, 645.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.39 (dd, J = 8.3, 0.7 Hz, 1 H), 7.84 (app t, J = 6.8 Hz, 2 H), 7.62 (dd, J = 7.2, 1.2 Hz, 1 H), 7.61 (td, J = 6.9, 1.4 Hz, 1 H), 7.53 (app t, J = 6.9 Hz, 1 H), 7.42 (dd, J = 8.3, 7.2 Hz, 1 H), 0.39 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.39, 133.06, 130.78, 128.95, 128.23, 126.80, 126.35, 126.17, 125.07, 120.73, 103.11, 99.39, 0.12.

1-*tert*-Butyl-4-(2'-trimethylsilylethynyl)benzene. Trimethylsilylacetylene (1.70 mL, 0.012 mol) was coupled with 1-bromo-4-*tert*-butylbenzene (1.70 mL, 9.80 mmol) as described in the Pd-catalyzed coupling procedure above using ether (8.0 mL), *n*-butyllithium (8.0 mL, 1.59 M in hexane, 0.0127 mol), zinc(II) chloride (2.38 g, 0.0175 mol), THF (7 mL), triphenylphosphine (0.18 g, 0.686 mmol), bis(dibenzylideneacetone)palladium(0) (0.12 g, 0.209 mmol) and THF (7 mL) overnight to afford 1.96 g (87%) of the title compound as a colorless oil. IR (neat) 3087.2, 3035.9, 2964.1, 2953.8, 2902.6, 2153.8, 1502.6, 1461.5, 1400.0, 1364.1, 1251.3, 1112.8, 1020.5, 866.7, 841.0, 759.0, 692.3, 620.5 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (1/2 AB q, J = 8.7 Hz, 2 H), 7.29 (1/2 AB q, J = 8.7 Hz, 2 H), 1.29 (s, 9 H), 0.23 (s, 9 H).

1-(9'-Anthracenyl)-2-trimethylsilylethyne. Trimethylsilylacetylene (1.70 mL, 0.012 mol) was coupled with 9-bromoanthracene (2.57 g, 9.99 mmol) as described in the Pd-catalyzed coupling procedure above using ether (8.0 mL), *n*-butyllithium (8.20 mL, 1.59 M in hexane, 0.0130 mol), zinc(II) chloride (2.31 g, 0.0169 mol), THF (8 mL), triphenylphosphine (0.17 g, 0.648 mmol), bis(dibenzylideneacetone)palladium(0) (0.11 g, 0.191 mmol) and THF (8 mL) to afford 2.29 g (84%) of the title compound as a red solid. IR (KBr) 3048.3, 2953.8, 2140.2, 1435.5, 1413.7, 1348.3, 1246.6, 1072.2, 1050.4, 1006.8, 839.7, 759.8, 730.8, 650.9, 614.5 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 8.7, 1.0 Hz, 2 H), 8.40 (s, 1 H), 7.98 (d, J = 8.4 Hz, 2 H), 7.57 (td, J = 6.6, 1.3 Hz, 2 H), 7.48 (td, J = 6.6, 1.3 Hz, 2 H), 0.42 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.87, 131.01, 128.60, 127.86, 126.72, 126.64, 125.56, 117.07, 106.11, 101.67, 0.31.

1-Ethynyl-2-phenylbenzene. 1-Phenyl-2-(2'-trimethylsilylethynyl)benzene (1.71 g, 6.82 mmol) was desilylated as described above using ether (20 mL), methanol (20 mL), and potassium carbonate (3.0 g, 21 mmol) for 1 h to afford 0.92 g (76.2%) of the title compound as a yellow oil that was used without purification. IR (neat) 3282.0, 3056.4, 3025.6, 2102.5, 1471.8, 1446.1, 1425.6, 1261.5, 1159.0, 1102.6, 1076.9, 1051.3, 1010.2, 948.7, 917.9, 871.8, 841.0, 759.0, 733.0, 697.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 - 7.59 (m, 3 H), 7.47 - 7.39 (m, 5 H), 7.33 - 7.29 (m, 1 H), 3.04 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.39, 140.22, 133.84, 129.57, 129.21, 128.93, 127.95, 127.52, 126.96, 120.42, 83.07, 80.15.

1-Phenyl-4-ethynylbenzene. 1-Phenyl-4-(2'-(trimethylsilyl)ethynyl)benzene (2.20 g, 0.00879 mol)was desilylated as described above using ether (10 mL), methanol (20 mL) and potassium carbonate (2.5 g, 0.0181 mol) for 45 min to afford 1.44 g (92 %) of the title compound as a white solid. IR (KBr) 3271.8, 3025.6,1482.1, 1394.9, 1246.2, 1112.8, 1076.9, 1005.1, 841.0, 764.1, 728.2, 702.6, 651.5, 625.6 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 2 H), 7.55 (s, 4 H), 7.44 (t, J = 7.0 Hz, 2 H), 7.36 (d, J = 7.3 Hz, 1 H), 3.11 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.55, 140.23, 132.54, 128.86, 127.72, 127.04, 126.99, 120.95, 83.53, 77.74.

1'-Naphthylethyne. 1-(1'-Naphthyl)-2-trimethylsilylethyne (1.80 g, 8.02 mmol) was desilylated as described above using ether (25 mL), methanol (30 mL), and potassium carbonate (2.5 g, 18 mmol) for 1 h to afford 1.06 g (87%) of the title compound as a yellow oil without purification. IR (neat) 3292.3, 3056.4, 2102.6, 1584.6, 1507.7, 1389.7, 1333.3, 1266.7, 1205.1, 1015.4, 800.0, 774.4, 646.2, 610.3 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.37 (dd, J = 8.2, 0.8 Hz, 1 H), 7.85 (d, J = 7.5 Hz, 2 H), 7.74 (dd, J = 7.1, 1.1 Hz, 1 H), 7.59 (td, J = 8.2, 1.5 Hz, 1 H), 7.52 (td, J = 6.8, 1.3 Hz, 1 H), 7.42 (dd, J = 8.3, 7.1 Hz, 1 H), 3.48 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.49, 133.06, 131.20, 129.24, 128.27, 126.92, 126.46, 126.03, 125.06, 119.75, 81.95, 81.74.

1-*tert*-Butyl-4-ethynylbenzene. 1-*tert*-Butyl-4-(2'-trimethylsilylethynyl)benzene (1.96 g) was desilylated as described above using ether (10 mL), methanol (30 mL), and potassium carbonate (3.0 g, 21 mmol) for 1 h to afford 1.06 g (79%) of the title compound as a yellow oil. IR (neat) 3296.9, 3089.7, 3037.9, 2985.4, 2955.1, 2105.6, 1503.8, 1462.4, 1395.0, 1363.9, 1270.7, 1203.4, 1105.0, 1016.9, 835.6, 644.0 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.42 (1/2 AB q, J = 8.5 Hz, 2 H), 7.29 (1/2 AB q, J = 8.5 Hz, 2 H), 3.01 (s, 1 H), 1.30 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.31, 132.12, 125.55, 119.36, 84.07, 77.51, 35.04, 31.40.

1-(9'-Anthracenyl)ethyne. 1-(9'-Anthracenyl)-2-trimethylsilylethyne was desilylated as described above using ether (20 mL), methanol (25 mL), and potassium carbonate (2.5 g, 18 mmol) for 1 h to afford 1.30 g (77%) of the title compound as a yellow oil. IR (neat) 3292.3, 3056.4, 2092.3, 1620.5, 1517.9, 1441.0, 1410.3, 1343.6, 1282.1, 1261.8, 1225.6, 1159.0, 1015.4, 953.8, 887.2, 846.2, 784.6, 733.3 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, J = 8.6, 0.8 Hz, 2 H), 8.43 (s, 1 H), 7.99 (d, J = 8.5 Hz, 2 H), 7.57 (td, J = 6.6, 1.3 Hz, 2 H), 7.49 (td, J = 6.6, 1.1 Hz, 2 H), 3.97 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.12, 130.95, 128.62, 128.18, 126.77, 126.50, 125.60, 115.97, 88.17, 80.36.

Z-1-Chloro-4-trimethylsilylbut-1-ene-3-yne.[11] Z-1,2-Dichloroethylene (6.00 mL, 0.0800 mol) and trimethylsilylacetylene (3.70 mL, 0.0262 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using benzene (50 mL), *n*-butylamine (3.00 mL, 0.0273 mol), tetrakis(triphenylphosphine)palladium(0) (0.45 g, 0.389 mol) and copper(I) iodide (0.20 g, 1.05 mol) overnight to afford 3.30 g (79%) of the title compound as a light brown oil. IR (neat) 3087.2, 3025.6, 2964.1, 2902.6, 2153.8, 1620.5, 1594.9, 1574.4, 1338.5, 1251.3, 1035.9, 1010.3, 846.2, 789.7, 759.0, 723.1, 661.5, 630.8. cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.37 (d, J = 7.5 Hz, 1 H), 5.86 (d, J = 7.5 Hz, 1 H), 0.21 (s, 9 H). ^{13}C (75 MHz, $CDCl_3$) δ 129.26, 112.11, 103. 77, 98.17, -0.24.

Z-4-Chloro-1-(2'-biphenyl)but-3-ene-1-yne. 1-Ethynyl-2-phenylbenzene (1.71 g, 9.59 mmol) was coupled with Z-1,2-dichloroethylene (2.70 mL, 0.0358 mol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.18 g, 0.959 mmol), triphenylphosphine (0.44 g, 1.68 mmol), benzene (15 mL), *n*-butylamine (2.80 mL, 0.0283 mol) and bis(dibenzylideneacetone)palladium(0) (0.27 g, 0.480 mmol) for 1 day to afford 1.67g (73%) of the title compound as a white solid. IR (neat) 3056.4, 3025.6, 2194.9, 1620.5, 1584.6, 1471.8, 1430.8, 1333.3, 1184.6, 1159.0, 1112.8, 1071.8, 1051.3, 1005.1, 984.6, 912.8, 810.3, 723.1, 687.2 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.2 Hz, 3 H), 7.43 - 7.27 (m, 6 H), 6.32 (d, J = 7.4 Hz, 1 H), 5.95 (d, J = 7.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.83, 140.17, 133.47, 129.59, 129.25, 128.99, 128.14, 128.04, 127.45, 127.00, 121.05, 112.18, 97.00, 86.16.

Z-4-Chloro-1-(4'-biphenyl)but-3-ene-1-yne. 1-Phenyl-4-ethynylbenzene (2.23 g, 0.012 mol) was coupled with Z-1,2-dichloroethylene (2.70 mL, 0.0358 mol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.23 g, 1.21 mmol), triphenylphosphine (0.33 g, 1.26 mmol), benzene (12 mL), *n*-butylamine (4.10 mL, 0.0486 mol) and bis(dibenzylideneacetone)palladium(0) (0.21 g, 0.365 mmol) for 1 day to afford 2.20 g (77%) of the title compound as a white solid. IR (KBr) 3076.9, 3025.6, 2194.9, 1584.6, 1482.1, 1446.2, 1400.0, 1333.2, 1112.8, 1005.1, 979.5, 841.0, 810.3, 764.1, 717.9, 687.2, 671.8, 630.8 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 - 7.61 (m, 6 H), 7.48 (br t, J = 7.3 Hz, 2 H), 7.42 - 7.39 (m, 1 H), 6.47 (d, J = 7.4 Hz, 1 H), 6.14 (d, J = 7.4 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.38, 140.11, 132.09, 128.81, 128.18, 127.66, 126.95, 126.94, 121.53, 112.08, 97.37, 83.98.

Z-4-Chloro-1-(1'-naphthyl)but-3-ene-1-yne. 1'-Naphthylethyne (1.75 g, 11.5 mmol) was coupled with Z-1,2-dichloroethylene (2.60 mL, 0.0346 mol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.22 g, 1.16 mmol), triphenylphosphine (0.36 g, 1.37 mmol), benzene (12 mL), *n*-butylamine (2.90 mL, 0.0293 mol) and bis(dibenzylideneacetone)palladium(0) (0.20 g, 0.348 mmol) for 1 day to afford 2.10 g (86%) of the title compound as a white solid. IR (neat) 3085.7, 3053.6, 2199.0, 1586.7, 1506.6, 1394.4, 1330.3, 1100.6, 1015.1, 956.4, 844.2, 796.1, 769.4, 716.0, 673.2, 630.5

cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.46 (d, J = 8.3 Hz, 1 H), 7.84 (dd, J = 7.6, 0.6 Hz, 2 H), 7.73 (dd, J = 7.1, 1.1 Hz, 1 H), 7.59 (td, J = 6.8, 1.5 Hz, 1 H), 7.52 (td, J = 6.8, 1.5 Hz, 1H), 7.43 (dd, J = 8.3, 7.4 Hz, 1 H), 6.51 (d, J = 7.4, 1 H), 6.23 (d, J = 7.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 133.13, 133.12, 130.71, 129.32, 128.41, 128.24, 127.01, 126.50, 126.23, 125.18, 120.39, 112.28, 95.66, 88.19.

Z-4-Chloro-(1'-(4'-*tert*-butyl)phenyl)but-3-ene-1-yne. 4-*tert*-Butylethynylbenzene (1.06 g, 6.70 mmol) was coupled with *Z*-1,2-dichloroethylene (1.50 mL, 0.0199 mol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.12 g, 0.631 mmol) triphenylphosphine (0.19 g, 0.724 mmol), benzene (7 mL), *n*-butylamine (2.60 mL, 0.0263 mol) and bis(dibenzylideneacetone)palladium(0) (0.12 g, 0.209 mmol) for 1 day to afford 2.10 g (86%) of the title compound as a yellow oil. IR (neat) 3087.2, 3035.9, 2964.1, 2871.8, 2205.1, 1615.4, 1584.6, 1502.6, 1461.5, 1394.9, 1364.1, 1338.5, 1266.7, 1107.7, 1020.5, 835.9, 805.1, 717.9, 656.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (1/2 AB q, J = 8.7 Hz, 2 H), 7.36 (1/2 AB q, J = 8.7 Hz, 2 H), 6.40 (d, J = 7.4 Hz, 1 H), 6.08 (d, J = 7.4 Hz, 1 H), 1.32 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.05, 131.44, 127.78, 125.34, 119.73, 112.24, 97.68, 82.71, 34.79, 31.12.

Z-4-Chloro-1-(9'-anthracenyl)but-3-ene-1-yne. (9'-Anthracenyl)ethyne (1.30 g, 6.43 mmol) was coupled with Z-1,2-dichloroethylene (1.60 mL, 0.0213 mol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.12 g, 0.631 mmol) triphenylphosphine (0.18 g, 0.686 mmol), benzene (10 mL), *n*-butylamine (1.90 mL, 0.0192 mol) and bis(dibenzylideneacetone)palladium(0) (0.11 g, 0.191 mmol) for 1 day to afford 1.34 g (79.6%) of the title compound as an orange solid. IR (KBr) 3087.2, 3046.2, 2184.6, 1656.4, 1630.8, 1405.1, 1117.9, 1010.3, 948.7, 876.9, 835.9, 779.5, 764.1, 723.1, 702.6, 666.7, 615.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (dd, J = 8.7, 0.8 Hz, 2 H), 8.42 (s, 1 H), 7.98 (d, J = 8.4 Hz, 2 H), 7.59 (td, J = 6.7, 1.3 Hz, 2 H), 7.49 (td, J = 6.6, 1.2 Hz, 2 H), 6.58 (d, J = 7.4 Hz, 7.4 Hz, 1 H), 6.41 (d, J = 7.4 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.74, 131.09, 128.65, 128.44, 128.26, 126.88, 126.71, 125.73, 116.67, 112.48, 94.62, 94.46.

Z-1-Trimethylsilyldodeca-3-ene-1,5-diyne. Crude *Z*-1-Chloro-4-(trimethylsilyl)but-1-ene-3-yne obtained above (about 0.013 mol) and 1-octyne (2.60 mL, 0.0176 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using benzene (35 mL), *n*-butylamine (3.00 mL, 0.0304 mol), copper(I) iodide (0.30 g, 1.58 mol) and tetrakis(triphenylphosphine)palladium(0) (0.60 g, 0.519 mol) overnight. The resulting oil was filtered through silica gel with hexane and taken on crude. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83-5.71 (m, 2 H), 2.38 (m, 2 H), 1.54 (m, 2 H), 1.40 (m, 2 H), 1.28 (m, 4 H), 0.87 (t, J = 6.8 Hz, 3 H).

Z-1-Trimethylsilyl-6-phenylhexa-3-ene-1,5-diyne. *Z*-1-Chloro-4-(trimethylsilyl)but-1-ene-3-yne (3.65 g, 0.0230 mol) and phenylacetylene (2.50 mL, 0.0228 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using benzene (25 mL), *n*-butylamine (3.50 mL, 0.0354 mol), tetrakis(triphenylphosphine)palladium(0) (0.85 g, 0.736 mmol) and copper(I) iodide (0.44 g, 2.31 mmol) for 1 day. The resulting oil was filtered through silica gel with hexane and was taken on crude. IR (neat) 3052.9, 2954.8, 2900.3, 2192.0, 2148.4, 1654.6, 1600.1, 1491.2, 1442.1, 1392.4, 1252.6, 1048.3, 956.9, 844.0, 752.6, 688.1 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (m, 2 H), 7.32 (m, 3 H), 6.04 (d, J = 10.9 Hz, 1 H), 5.86 (d, J = 10.9 Hz, 1 H), 0.23 (s, 9 H).

1,2-Bis(2'-trimethylsilylethynyl)benzene. 1,2-Dibromobenzene (1.60 mL, 0.0133 mol) and trimethylsilylacetylene (4.00 mL, 0.0283 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using benzene (30 mL), *n*-butylamine (4.00 mL, 0.0408 mol), tetrakis(triphenylphosphine)palladium(0) (0.96 g, 0.831 mmol) and copper(I) iodide (0.21 g, 1.10 mmol) for 1 day at room temperature and then at 70°C for 2 day. The red brown oil was purified by distillation (175°C, 4 mm Hg). The resultant oil was further purified by chromatography (silica gel, hexane) to yield 2.83 g (79%) of the title compound as a yellow oil. IR (neat) 3062.4, 2960.4, 2899.7, 2161.3, 1474.5, 1441.3, 1408.1, 1249.5, 1228.4, 1201.0, 1099.6, 1037.9, 950.0, 866.1, 842.0, 758.3, 699.7, 642.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (dd, J = 5.8, 3.4 Hz, 2 H), 7.21 (dd, J = 5.8, 3.3 Hz, 2 H), 0.25 (s, 18 H). ^{13}C (75 MHz, $CDCl_3$) δ 132.28, 128.03, 125.74, 103.20, 98.42, 0.03.

Z-1,6-Bis(trimethylsilyl)hexa-3-ene-1,5-diyne.[12] 1,2-Dichloroethylene (1.00 mL, 0.0133 mol) and trimethylsilylacetylene (4.00 mL, 0.0283 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using benzene (30 mL), *n*-butylamine (4.00 mL, 0.0408 mol), tetrakis(triphenylphosphine)palladium(0) (0.90 g, 0.779 mmol) and copper(I) iodide (0.19 g, 0.999 mmol) for 2 day to yield 1.90 g (64.8%) of the title compound as a light brown oil after distillation (125°C, 4.5 mm Hg). IR (neat) 2961.0, 2889.8, 2156.2, 1250.8, 1070.4, 977.9, 844.5, 760.0, 700.0, 635.6 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 5.83 (s, 2 H), 0.21 (s, 18 H). ^{13}C (125 MHz, CDCl$_3$) δ 120.58, 103.38, 101.83, -0.13.

Z-1-Trimethylsilyl-6-(2'-biphenyl)hexa-3-ene-1,5-diyne. *Z*-4-Chloro-1-(2'-biphenyl)but-3-ene-1-yne (1.67 g, 7.00 mmol) was coupled with trimethylsilylacetylene (1.50 mL, 10.6 mmol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.14 g, 0.736 mmol), triphenylphosphine (0.32 g, 1.22 mmol), benzene (8 mL), *n*-butylamine (2.80 mL, 0.0283 mol) and bis(dibenzylideneacetone)palladium(0) (0.20 g, 0.348 mmol) for 1 day to afford 1.89 g (90%) of the title compound as a yellow oil. IR (neat) 3056.4, 3025.6, 2953.8, 2194.9, 2143.6, 1948.7, 1702.6, 1682.1, 1594.9, 1574.4, 1476.9, 1451.3, 1430.8, 1389.7, 1251.3, 1112.8, 1056.4, 1041.0, 1010.3, 953.8, 846.2, 753.8, 697.4, 635.9 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.67 - 7.61 (m, 3 H), 7.44 - 7.27 (m, 6 H), 5.91 (d, J = 11.0 Hz, 1 H), 5.80 (d, J = 11.0 Hz, 1 H), 0.23 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 143.57, 140.21, 133.76, 129.53, 129.22, 128.90, 127.99, 127.47, 126.91, 121.32, 120.70, 118.96, 102.96, 102.27, 97.33, 89.91, -0.08.

Z-1-Trimethylsilyl-6-(4'-biphenyl)hexa-3-ene-1,5-diyne. *Z*-4-Chloro-1-(4'-biphenyl)but-3-ene-1-yne (2.08 g, 8.71 mmol) was coupled with trimethylsilylacetylene (1.80 mL, 12.7 mmol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.17 g, 0.894 mmol), triphenylphosphine (0.39 g, 1.49 mmol), benzene (10 mL), *n*-butylamine (2.50 mL, 0.0253 mol) and bis(dibenzylideneacetone)palladium(0) (0.25 g, 0.435 mmol) for 1 day to afford 1.70 g (65%) of the title compound as a yellow oil. IR (neat) 3033.3, 2955.6, 2188.9, 2133.3, 1483.3, 1400.0, 1250.0, 1050.0, 950.0, 838.9, 761.1, 694.4, 633.3, 561.1, 494.4, 461.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.63 - 7.54 (m, 6 H), 7.46 (br t, J = 7.0 Hz, 1 H), 7.40 - 7.35 (m, 1 H), 6.11 (d, J = 10.9 Hz, 1 H), 5.93 (d, J = 10.9 Hz, 1 H), 0.31 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 141.30, 140.15, 132.19, 128.82, 127.67, 126.96, 121.90, 120.69, 119.29, 103.39, 102.28, 97.55, 87.85, -0.08.

Z-1-Trimethylsilyl-6-(1'-naphthyl)hexa-3-ene-1,5-diyne. *Z*-4-Chloro-1-(1'-naphthyl)but-3-ene-1-yne (1.01 g, 4.75 mmol) was coupled with trimethylsilylacetylene (1.00 mL, 7.08 mmol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.10 g, 0.526 mmol), triphenylphosphine (0.22 g, 0.839 mmol), benzene (5 mL), *n*-butylamine (1.50 mL, 0.0152 mol) and bis(dibenzylideneacetone)palladium (0.14 g, 0.244 mmol) for 1 day to afford 0.68 g (53%) of the title compound as a yellow oil. IR (neat) 3055.6, 2961.1, 2895.7, 2191.0, 2140.2, 1675.2, 1588.0, 1508.1, 1404.5, 1331.2, 1250.4, 1103.7, 1059.7, 1030.3, 934.9, 846.9, 795.5, 766.2, 700.1, 656.1, 634.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.46 (d, J = 7.7 Hz, 1 H), 7.83 (d, J = 7.3 Hz, 2 H), 7.70 (dd, J = 7.1, 1.0 Hz, 1 H), 7.53 (td, J = 7.6, 1.5 Hz, 1 H), 7.43 (dd, J = 8.2, 7.3 Hz, 2 H), 6.19 (d, J = 11.0 Hz, 1 H), 5.94 (d, J = 11.0 Hz, 1 H), 0.25 (s, 9 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 133.64, 133.59, 131.48, 129.73, 128.71, 127.41, 126.92, 126.86, 125.70, 121.21, 121.03, 119.59, 104.01, 103.00, 96.21, 92.38, 0.50.

Z-1-Trimethylsilyl-6-(4'-(*tert*-butyl)phenyl)hexa-3-ene-1,5-diyne. *Z*-4-Chloro-(1'-(4'-*tert*-butyl)phenyl)but-3-ene-1-yne (1.63 g, 7.45 mmol) was coupled with trimethylsilylacetylene (1.50 mL, 1.06 mmol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.13 g, 0.684 mmol), triphenylphosphine (0.32 g, 1.22 mmol), benzene (6 mL), *n*-butylamine (2.80 mL, 0.0283 mol), and bis(dibenzylideneacetone)palladium(0) (0.20 g, 0.348 mmol) for 1 day to afford 0.88 g (65 %) of the title compound as a yellow oil. IR (neat) 3084.8, 3040.8, 2960.1, 2901.4, 2864.7, 2197.0, 2145.6, 1676.0, 1566.0, 1499.9, 1463.2, 1397.2, 1360.5, 1250.4, 1199.1, 1111.0, 1052.3, 956.9, 839.5, 758.8, 700.1, 634.1 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.39 (1/2 AB q, J = 8.7 Hz, 2 H), 7.32 (1/2 AB q, J = 8.7 Hz, 2 H), 6.04 (d, J = 10.9 Hz, 1 H), 5.83 (d, J = 10.9 Hz, 1 H), 1.30 (s, 9 H), 0.23 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 151.91, 131.55, 125.30, 120.89, 120.08, 118.78, 102.98, 102.35, 97.91, 86.59, 34.77, 31.13, -0.07.

Z-1-Trimethylsilyl-6-(9'-anthracenyl)hexa-3-ene-1,5-diyne. *Z*-4-Chloro-1-(9'-anthracenyl)but-3-ene-1-yne (1.34 g, 5.12 mmol) was coupled with trimethylsilylacetylene (1.50 mL, 1.06 mmol) as described in the Pd/Cu-catalyzed coupling procedure above using copper(I) iodide (0.10 g, 0.526 mmol), triphenylphosphine (0.14 g, 0.534 mmol), benzene (5 mL), *n*-butylamine (2.00 mL, 0.0202 mol) , and bis(dibenzylideneacetone)palladium(0) (0.09 g, 0.157 mmol) for 1 day to afford 0.88 g (42 %) of the title compound as an orange oil. IR (neat) 3046.2, 2953.8, 2174.4, 2133.3, 1620.5, 1569.2, 1517.9, 1441.0, 1415.4, 1251.3, 1123.1, 1025.6, 887.2, 846.2, 759.0, 738.5, 630.6, 615.4 cm^{-1}. ^{1}H NMR (300 MHz,

$CDCl_3$) δ 8.65 (d, J = 8.7 Hz, 2 H), 8.43 (s, 1H), 7.99 (d, J = 8.3 Hz, 2 H), 7.56 (td, J = 6.7, 1.4 Hz, 2 H), 7.49 (td, J = 6.6, 1.4 Hz, 2 H), 6.37 (d, J = 11.0 Hz, 1 H), 6.01 (d, J = 11.0 Hz, 1 H), 0.28 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132.77, 131.13, 128.65, 128.45, 126.87, 126.85, 125.71, 120.43, 118.65, 103.83, 102.71, 98.34, 94.41, 0.11.

1-(2'-Trimethylsilylethynyl)-2-(2''-phenylethynyl)benzene. Phenylacetylene (1.10 mL, 10.0 mmol) was coupled with 1,2-dibromobenzene (1.20 mL, 9.95 mmol) as described in the Pd-catalyzed coupling procedure above using ether (10.0 mL), *n*-butyllithium (6.20 mL, 1.65 M in hexane, 10.20 mmol), zinc(II) chloride (2.04 g, 0.0150 mol), THF (5 mL), triphenylphosphine (0.27 g, 1.03 mmol), bis(dibenzylideneacetone)palladium(0) (0.17 g, 0.296 mmol) and THF (5 mL) overnight to generate 1-bromo-2-(2'-phenylethynyl)benzene. Then the resulting 1-bromo-2-(2'-phenylethynyl)benzene was coupled with trimethylsilylacetylene (1.80 mL, 0.0127 mol) as described in the Pd-catalyzed coupling procedure above using ether (8.0 mL), *n*-butyllithium (7.80 mL, 1.65 M in hexane, 0.0129 mol), zinc(II) chloride (2.36 g, 0.0170 mol), THF (15 mL), triphenylphosphine (0.40 g, 1.53 mmol), bis(dibenzylideneacetone)palladium(0) (0.17 g, 0.296 mmol) and THF (6 mL) overnight to afford the title compound as a colorless oil which was used directly for the next step. ^1H NMR (300 MHz, $CDCl_3$) δ 7.56 - 7.53 (m, 2 H), 7.51 - 7.47 (m, 2 H), 7.34 - 7.31 (m, 3 H), 7.28 - 7.23 (m, 2 H), 0.25 (s, 9 H).

Z-1,5-Dodecadiyn-3-ene. Crude *Z*-1-(trimethylsilyl)dodeca-3-ene-1,5-diyne obtained above (about 0.013 mol) was desilylated as described above using potassium carbonate (2.00 g, 0.0145 mol), methanol (10 mL) and ether (5 mL) 2 h to yield 0.32 g (15% based on *Z*-1,2-dichloroethylene) of the title compound as a yellow oil. IR (neat) 3292.8, 2930.8, 2858.5, 2275.7, 2210.5, 2096.4, 1575.3, 1465.9, 1390.2, 1327.1, 1250.3, 1136.3, 853.4, 746.9, 612.6 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (app d, J = 10.9 Hz, 1 H), 5.70 (dd, J = 10.9, 2.3 Hz, 1 H), 3.27 (dd, J = 2.3, 0.9 Hz, 1 H), 2.38 (dt, J = 6.6, 2.2 Hz, 2 H), 1.54 (m, 2 H), 1.42 (m, 2 H), 1.28 (m, 4 H), 0.87 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.44, 116.90, 99.64, 83.64, 80.90, 77.81, 31.32, 28.50, 28.45, 22.53, 19.74, 14.02.

Z-1-Phenylhexa-3-ene-1,5-diyne. Crude *Z*-1-trimethylsilyl-6-phenylhexa-3-ene-1,5-diyne obtained above (about 0.035 mol) was desilylated as described above using potassium carbonate (2.00 g, 0.0145 mol), methanol (10 mL) and ether (5 mL) for 2 h to yield 2.09 g (39% based on Z-1,2-dichloroethylene) of the title compound as a yellow oil. IR (neat) 3289.7, 3046.8, 2925.3, 2205.0, 2094.0, 1681.9, 1597.3, 1571.1, 1488.2, 1442.0, 1391.8, 1266.0, 1069.8, 1030.5, 916.5, 755.4, 689.5, 622.3 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 2 H), 7.33 (m, 3 H), 6.13 (dd, J = 10.0, 0.9 Hz, 1 H), 5.84 (dd, J = 10.7, 2.4 Hz, 1 H), 3.40 (dd, J = 2.4, 0.9 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.84, 128.74, 128.31, 122.82, 121.62, 118.21, 97.52, 86.48, 85.02, 80.81.

1,2-Diethynylbenzene. 1,2-Bis(2'-trimethylsilylethynyl)benzene (3.60 g, 0.0133 mol) was desilylated as described above using potassium carbonate (2.0 g, 0.0145 mol), THF (7 mL) and methanol (5 mL) for 2 h to yield 1.12 g (67%) of the title compound as a yellow oil after distillation (100°C, 7 mm Hg). IR (neat) 3287.9, 1475.2, 1439.1, 1249.9, 1092.4, 1036.0, 953.0, 808.6, 759.1, 668.0, 618.0 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (dd, J = 5.7, 3.4 Hz, 2 H), 7.21 (dd, J = 5.8, 3.3 Hz, 2 H), 3.32 (s, 2 H). ^{13}C (125 MHz, $CDCl_3$) δ 132.58, 128.47, 124.99, 81.78, 81.64. HRMS calculated for $C_{10}H_6$: 126.0470. Found: 126.0472.

1,2-Bis(2'-phenylethynyl)benzene. 1,2-Dibromobenzene (1.80 mL, 0.0149 mol) and phenylacetylene (3.70 mL, 0.0337 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using THF (50 mL), *iso*-propylamine (7.00 mL, 0.0499 mol), copper(I) iodide (0.32 g, 1.68 mmol) and bis(triphenylphosphine)palladium(II) chloride (0.96 g, 0.831 mmol) at 100°C for 5 day to yield 2.21 g (53%) of the title compound as a yellow oil that later solidified. IR (KBr) 3057.4, 2212.9, 1596.5, 1492.4, 1441.0, 1317.8, 1272.4, 1176.4, 1089.8, 1068.4, 1024.1, 952.2, 911.5, 754.7, 688.5 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.55 (m, 6 H), 7.31 (m, 8 H). ^{13}C (75 MHz, $CDCl_3$) δ 131.76, 131.63, 128.40, 128.34, 127.98, 125.79, 123.26, 93.57, 88.29. HRMS calculated for $C_{22}H_{14}$: 278.1095. Found: 278.1091.

1,2-Di(1'-octynyl)benzene. 1-Octyne (3.00 mL, 0.0203 mol) and 1,2-dibromobenzene (1.20 mL, 9.95 mmol) were coupled as described in the Pd-catalyzed coupling procedure above using *n*-butyllithium (13.50 mL, 1.5 M in hexane, 0.0203 mol), ether (15 mL), zinc(II) chloride (3.25 g, 0.0238 mol), THF (10 mL), tris(dibenzylideneacetone)bispalladium chloroform (0.34 g, 0.328 mmol), triphenylphosphine (0.69 g, 2.63 mmol), tetrakis(triphenylphosphine)palladium(0) (0.104 g, 0.090 mmol) and THF (10 mL) for 7 day to yield 1.27 g (43%) of the title compound as a yellow oil. IR (neat) 3060.0, 2930.3, 2857.7, 2228.2, 1481.1, 1466.4, 1442.5, 1377.9, 1329.9, 1106.0, 946.2, 756.0 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (dd, J = 5.7, 3.5 Hz, 2 H), 7.14 (dd, J = 5.8, 3.4 Hz, 2 H), 2.43 (t, J = 7.1 Hz, 4 H), 1.64-1.58 (m, 4 H), 1.49-143 (m, 4 H), 1.34-1.25 (m, 8 H), 0.88 (t, J = 7.0 Hz, 6 H). ^{13}C (125 MHz, $CDCl_3$) δ 131.76, 127.07, 126.35, 94.14, 79.55, 31.45, 28.81, 28.62, 22.58, 19.68, 14.08. HRMS calculated for $C_{22}H_{30}$: 294.2347. Found: 294.2357.

Z-7,11-Octadeca-9-enediyne. Z-1,2-Dichloroethylene (1.90 mL, 0.0252 mol) and 1-octyne (7.80 mL, 0.0529 mol) were coupled as described in the Pd/Cu-catalyzed coupling procedure above using benzene (50 mL), *n*-butylamine (8.00 mL, 0.0809 mol), tetrakis(triphenylphosphine)palladium(0) (1.64 g, 1.42 mol) and copper(I) iodide (0.41 g, 2.15 mol) for 4 day to yield 3.18 g (52%) of the title compound as a light brown oil after distillation (160°C, 4.0 mm Hg). IR (neat) 2931.0, 2858.4, 2215.9, 1466.0, 1327.3, 743.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (s, 2 H), 2.37 (t, J = 6.9 Hz, 4 H), 1.53 (m, 4 H), 1.40 (m, 4 H), 1.28 (m, 8 H), 0.87 (t, J = 6.9 Hz, 6 H). ^{13}C (75 MHz, $CDCl_3$) δ 118.89, 97.92, 78.23, 31.39, 28.65, 28.54, 22.55, 19.78, 14.06.

Z-1-(2'-Biphenyl)hexa-3-ene-1,5-diyne. Z-1-Trimethylsilyl-6-(2'-biphenyl)hexa-3-ene-1,5-diyne (3.36 g, 0.0111 mole) was desilylated as described above using ether (5 mL), methanol (30 mL), and potassium carbonate (3.5 g, 26 mmol) for 1 h to afford the title compound in quantitative yield as a yellow oil. IR (neat) 3282.1, 3056.4, 2194.9, 2092.3, 1476.9, 1430.8, 1389.7, 1251.3, 1159.0, 1112.8, 1076.9, 1015.4, 856.4, 753.8, 697.4 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 - 7.66 (m, 3 H), 7.48 - 7.38 (m, 5 H), 7.36 - 7.32 (m, 1 H), 6.04 (br d, J = 10.9 Hz, 1 H), 5.79 (dd, J = 10.9, 2.3 Hz, 1 H), 3.24 (dd, J = 2.3, 0.8 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.81, 140.30, 133.67, 129.57, 129.22, 128.96, 127.99, 127.35, 126.93, 121.63, 121.10, 117.88, 97.22, 89.29, 84.74, 80.71.

Z-1-(4'-Biphenyl)hexa-3-ene-1,5-diyne. Z-1-Trimethylsilyl-6-(4'-biphenyl)hexa-3-ene-1,5-diyne (0.65 g, 2.15 mmol) was desilylated as described above using ether (10 mL), methanol (20 mL), and potassium carbonate (2.5 g, 18 mmol) for 1 h to afford 0.32 g (65%) of the title compound as a yellow oil. IR (neat) 3292.3, 3271.8, 3035.9, 2194.9, 2092.3, 1482.1, 1400.0, 1112.8, 1076.9, 1005.1, 841.0, 764.1, 697.4, 656.4, 630.8 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 - 7.58 (m, 6 H), 7.46 (br t, J = 7.0 Hz, 2 H), 7.42 - 7.37 (m, 1 H), 6.17 (dd, J = 10.9, 0.9 Hz, 1 H), 5.88 (dd, J = 10.9, 2.4 Hz, 1 H), 3.46 (dd, J = 2.4, 0.9 Hz, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.41, 140.15, 132.25, 128.82, 127.68, 126.96, 121.64, 121.60, 118.16, 97.48, 87.22, 85.16, 80.86.

Z-1-(1'-Naphthyl)hexa-3-ene-1,5-diyne. Z-1-Trimethylsilyl-6-(1'-naphthyl)hexa-3-ene-1,5-diyne was desilylated as described above using ether (5 mL), methanol (30 mL), and potassium carbonate (3.5 g, 26 mmol) for 1 h to afford the title compound in quantitative yield as a yellow oil. IR (neat) 3292.3, 3046.2, 2184.6, 2092.3, 1684.6, 1584.6, 1507.7, 1400.0, 1246.2, 1100.0, 1015.4, 800.0, 769.2, 746.2, 623.1 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (br d, J = 7.7 Hz, 1 H), 7.83 (br d, J = 7.8 Hz, 2 H), 7.72 (dd, J = 7.2, 1.2 Hz, 1 H), 7.58 - 7.50 (m, 2 H), 7.43 (dd, J = 8.3, 7.2 Hz, 1 H), 6.28 (dd, J = 10.9, 0.9 Hz, 1 H), 5.93 (dd, J = 10.8, 2.4 Hz, 1 H), 3.51 (dd, J = 2.4, 0.9 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.22, 133.15, 130.91, 129.41, 128.27, 126.87, 126.51, 126.47, 125.25, 121.89, 120.54, 118.28, 95.72, 91.52, 85.25, 81.40.

Z-1-(4'-(*tert*-Butyl)phenyl)hexa-3-ene-1,5-diyne. Z-1-Trimethylsilyl-6-(4'-(*tert*-butyl)phenyl)hexa-3-ene-1,5-diyne (0.88 g, 3.14 mmol) was desilylated as described above using ether (5 mL), methanol (10 mL), and potassium carbonate (2.0 g, 14 mmol) for 1 h to afford 0.53 g (81 %) of the title compound as a yellow oil. IR (neat) 3294.6, 3036.6, 2960.8, 2869.8, 2202.2, 2096.0, 1678.8, 1572.6, 1504.4, 1458.9, 1390.6, 1360.3, 1269.2, 1201.0, 1109.9, 1026.5, 836.9, 745.8, 632.1 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 (1/2 ABq, J = 8.6 Hz, 2 H), 7.35 (1/2 ABq, J = 8.6 Hz, 2 H), 6.12 (dd, J = 10.9, 0.9 Hz, 1 H), 5.82 (dd, J = 10.9, 2.5 Hz, 1 H), 3.39 (dd, J = 2.5, 0.9 Hz, 1 H), 1.32 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.06, 131.58, 125.31, 121.81, 119.83, 117.76, 97.83, 86.00, 84.84, 80.91, 34.79, 31.12.

Z-1-(9'-Anthracenyl)hexa-3-ene-1,5-diyne. Z-1-Trimethylsilyl-6-(9'-anthracenyl)hexa-3-ene-1,5-diyne (1.54 g, 4.75 mmol) was desilylated as described above using ether (20 mL), methanol (20 mL), and potassium carbonate (3.0 g, 22 mmol) for 1 h to afford 0.69 g (58 %) of the title compound as a red orange oil that later solidified. IR (neat) 3292.3, 3046.2, 2174.4, 2092.3, 1620.5, 1569.2, 1517.9, 1441.0, 1415.4, 1389.7, 1348.7, 1261.5, 1123.1, 1015.4, 959.0, 887.2, 846.2, 784.6, 738.5, 615.4 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.69 (d, J = 7.8 Hz, 2 H), 8.43 (s, 1 H), 7.99 (d, J = 7.8 Hz, 2 H), 7.58 - 7.47 (m, 4 H), 6.44 (d, J = 10.9 Hz, 1 H), 5.98 (dd, J = 10.8, 2.3 Hz, 1 H), 3.60 (d, J = 2.4 Hz, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 132.80, 131.09, 128.65, 128.55, 126.90, 126.74, 125.72, 122.05, 117.91, 116.79, 98.02, 94.49, 85.46, 81.88.

1-(Ethynyl)-2-(2''-phenylethynyl)benzene. 1-(2'-Trimethylsilylethynyl)-2-(2''-phenylethynyl)benzene was desilylated as described above using methanol (50 mL), and potassium carbonate (5.0 g, 35 mmol) for 1 h to afford 0.40 g (20 % from 1,2-dibromobenzene) of the title compound as a yellow oil. IR (neat) 3286.1, 3059.2, 2213.5, 2110.4, 1596.3, 1570.5, 1493.1, 1472.5, 1441.6, 1090.9, 1070.3, 1023.9, 951.7, 915.6, 853.7, 755.7, 688.7, 621.7 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.58 - 7.51 (m, 4 H), 7.36 - 7.24 (m, 5 H), 3.36 (s, 1 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 132.62, 131.81, 128.57, 128.53, 128.37, 127.95, 126.35, 124.66, 123.18, 93.58, 87.89, 82.22, 81.17.

3-Bromo-4-(2'-phenylethynyl)thiophene. 3,4-Dibromothiophene (2.45 g, 0.0101 mol) and phenylacetylene (1.10 mL, 0.0100 mol) were coupled as described in the Pd-catalyzed coupling procedure above using ether (10 mL), *n*-butyllithium (6.30 mL, 1.6 M in hexane, 0.0101 mol), zinc(II) chloride (1.80 g, 0.0132 mol), THF (20 mL), triphenylphosphine (0.33 g, 0.00126 mol), bis(dibenzylideneacetone)palladium(0) (0.17 g, 0.296 mmol) and benzene (8 mL) for 1 day at room temperature and 1 day at 70°C. Since there was still some starting material left, another portion of the zinc reagent was prepared using phenylacetylene (0.30 mL, 0.00273 mol), ether (10 mL), *n*-butyllithium (1.80 mL, 1.6 M in hexane, 0.00288 mol), zinc(II) chloride (0.48 g, 0.00352 mol) and THF (5 mL). After adding the zinc reagent, the reaction was heated to 70°C for 1 day to afford 1.65 g (62%) of the title compound as a yellow oil. IR (neat) 3111.1, 3055.6, 1600.0, 1505.6, 1483.3, 1444.4, 1422.2, 1338.9, 1261.1, 1155.6, 1066.7, 1027.8, 983.3, 916.7, 872.2, 850.0, 788.9, 755.6, 688.9 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.54 (m, 2 H), 7.49 (d, J = 3.4 Hz, 1 H), 7.33 (m, 3 H), 7.26 (d, J = 3.4 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 132.10, 129.11, 128.97, 128.77, 125.02, 123.35, 123.20, 114.25, 92.61, 83.15.

3-(2'-Trimethylsilylethynyl)-4-(2''-phenylethynyl)thiophene. 3-Bromo-4-(2'-phenylethynyl)thiophene (1.10 g, 0.00418 mol) and trimethylsilylacetylene (0.90 mL, 0.00637 mol) were coupled as described in the Pd-catalyzed coupling procedure above using THF (5.0 mL), *n*-butyllithium (4.00 mL, 1.6 M in hexane, 0.00640 mol), zinc(II) chloride (1.20 g, 0.00880 mol), THF (10 mL) and tetrakistriphenylphosphinepalladium(0) (0.29 g, 0.251 mmol) at 70°C for 1 day to afford 1.16 g (99%) of the title compound as a yellow solid. IR (KBr) 3107.7, 2964.1, 2153.8, 1594.9, 1487.2, 1441.0, 1251.3, 1169.2, 1092.3, 871.8, 841.0, 805.1, 753.8, 692.3, 651.3 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.51 (m, 2 H), 7.43 (d, J = 3.1 Hz, 1 H), 7.40 (d, J = 3.1 Hz, 1 H), 7.31 (m, 3 H), 0.24 (s, 9 H). ^{13}C NMR (75 MHz, CDCl$_3$) δ 132.06, 129.42, 128.76, 128.75, 128.27, 125.62, 125.49, 123.62, 98.90, 97.30, 92.13, 83.67, 0.45.

3-(2'-Phenylethynyl)-4-ethynylthiophene. 3-(2'-Trimethyl-silylethynyl)-4-(2''-phenylethynyl)thiophene (1.16 g, 0.00414 mol) was desilylated as described above using methanol (25 mL), ether (15 mL) and potassium carbonate (3.0 g) to afford 0.80 g (69%) of the title compound as a yellow oil. IR (neat) 3292.3, 3107.7, 3056.4, 2215.4, 2112.8, 1594.9, 1487.2, 1441.0, 1343.6, 1153.8, 1071.8, 1025.6, 912.8, 866.7, 794.9, 753.8 cm^{-1}. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.53 (m, 2 H), 7.49 (d, J = 3.2 Hz, 1 H), 7.44 (d, J = 3.2 Hz, 1 H), 7.32 (m, 3 H), 3.21 (s, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 132.13, 130.15, 128.82, 128.71, 128.47, 125.50, 124.24, 123.40, 92.05, 83.21, 79.90, 77.77.

2,3-Dibromobenzothiophene.[13] A solution of bromine (3.20 mL, 0.0622 mol) in chloroform (10 mL) was added to benzothiophene (4.00 g, 0.0298 mol) in chloroform (20 mL) at 0°C overnight. After warming to room temperature, the reaction mixture was poured into aqueous sodium hydroxide and the organic phase was separated. Then the organic phase was twice washed with 3 N sodium hydroxide and once with water. After drying over magnesium sulfate, the solvent was removed *in vacuo*. The resulting pale yellow solid was purified by chromatography (silica gel, hexane) to afford 7.95 g (91%) of the title compound as a white solid. IR (KBr) 3055.6, 1493.6, 1450.0, 1420.9, 1297.4, 1239.3, 985.0, 897.9, 745.3, 716.2 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.74 (br t, J = 7.9 Hz, 2 H), 7.39 (br qn, J = 7.8 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$) δ 139.30, 137.91, 126.08, 125.94, 123.75, 122.25, 114.61, 112.11.

2,3-Bis(2'-trimethylsilylethynyl)benzothiophene. 2,3-Dibromobenzothiophene (2.00 g, 0.00685 mol) and trimethylsilylacetylene (2.20 mL, 0.0156 mol) were coupled as described in the Pd-catalyzed coupling procedure above using ether (15.0 mL), *t*-butyllithium (7.50 mL, 2.08 M in hexane, 0.0154 mol), zinc(II) chloride (3.00 g, 0.0220 mol), THF (15 mL) and bis(dibenzylideneacetone)palladium(0) (0.16 g, 0.278 mmol) and triphenylphosphine (0.33 g, 0.00126 mol) at 60°C for 1 day to afford 1.91 g (0.00618 mol, 90%) of 2-(2'-trimethylsilylethynyl)-3-bromobenzo-thiophene. This compound was immediately coupled with trimethylsilylacetylene (4.80 mL, 0.0340 mol) as described in the Pd-catalyzed coupling procedure above using ether (35.0 mL), *t*-butyllithium (16.50 mL, 2.08 M in hexane, 0.0343 mol), zinc(II) chloride (6.85 g, 0.0503 mol), THF (15 mL), bis(dibenzylideneacetone)palladium(0) (0.39 g, 0.678 mmol) and triphenylphosphine (0.89 g, 0.00339 mol) at 80°C for 2 day to afford 1.52 g (75%) of the title compound as yellow oil. IR (neat) 3062.8, 2961.1, 2895.7, 2147.4, 1428.2, 1348.3, 1319.2, 1246.6, 1195.7, 1159.4, 1072.2, 1035.9, 839.7, 759.8, 730.8, 701.7, 665.4, 636.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (m, 1 H), 7.70 (m, 1 H), 7.39 (m, 2 H), 0.30 (s, 9 H), 0.28 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.47, 138.30, 127.10, 126.39, 125.17, 123.79, 123.57, 122.09, 106.00, 101.95, 97.49, 96.87, 0.15, -0.09.

2,3-Di(ethynyl)benzothiophene. 2-Bis-(2'-trimethylsilylethynyl)benzothiophene (1.81 g, 0.00554 mol) was desilylated as described above using methanol (50 mL) and potassium carbonate (3.5 g, 0.025 mol) to afford 0.86 g (85%) of the title compound as a yellow oil that later solidified. IR (KBr) 3292.3, 3061.5, 2107.7, 1592.3, 1500.0, 1461.5, 1430.8, 1338.5, 1323.1, 1261.5, 1223.1, 1169.2, 1153.8, 1123.1, 1069.2, 1000.0, 938.5, 869.2, 753.8, 730.8, 607.7 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (m, 1 H), 7.70 (m, 1 H), 7.43 (m, 2 H), 3.77 (s, 1 H), 3.62 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.90, 138.78, 127.09, 126.85, 125.85, 123.92, 123.29, 122.55, 87.96, 84.67, 76.95, 76.68.

***tert*-Butyldimethylsilyl propargyl ether.** Propargyl alcohol (2.40 mL, 0.0412 mol), imidazole (6.20 g, 0.0911 mol), *tert*-butyldimethylsilyl chloride (7.45 g, 0.0494 mol) and methylene chloride (20 mL) were stirred together at room temperature for 30 min. After completion, the reaction mixture was poured into water and the organic phase was separated. The organic phase was then washed with dilute hydrochloric acid. The combined aqueous phases were extracted with ether and the combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuo. The resulting oil was purified by chromatography (hexane, silica) to yield 2.30 g (33%) of the title compound as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (d, J = 2.4 Hz, 2 H), 2.34 (t, J = 2.4 Hz, 1 H), 0.87 (s, 9 H), 0.08 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 82.80, 73.18, 51.88, 26.16, 18.65, -4.84.

***tert*-Butyldimethylsilyl (*E*)-3-iodo-2-propenyl ether.**[14] *tert*-Butyldimethylsilyl propargyl ether (5.35 g, 0.0314 mol), a trace of AIBN and tri-*n*-butyltin hydride (11.0 mL, 0.0409 mol) were heated together to 80°C for 2 h. After completion, methylene chloride was added and the reaction mixture was poured into water. After separation of the layers, the organic phase was twice washed with water. The combined aqueous phases were extracted with ether and the combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuo. The resulting oil was purified by chromatography (hexane, silica) to yield 12.50 g (86%) of the title compound as a colorless oil. This oil was immediately added to a solution of methylene chloride (50 mL) and iodine (7.60 g, 0.0299 mol). After stirring overnight at room temperature, the reaction mixture was washed three times with water. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. Purification by chromatography yielded 1.30 g (16%) of the title compound as a pink oil. IR (neat) 2950.9, 2930.3, 2858.4, 1607.1, 1473.5, 1463.2, 1370.7, 1257.7, 1165.2, 1129.2, 1098.4, 1052.2, 1005.9, 949.4, 934.0, 836.4, 774.7, 695.7 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.58 (dt, J = 14.3, 4.5 Hz, 1 H), 6.27 (dt, J = 14.3, 1.9 Hz, 1 H), 4.08 (dd, J = 4.5, 1.9 Hz, 2 H), 0.88 (s, 9 H), 0.05 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.95, 75.88, 65.38, 25.87, 18.36, -5.35.

***tert*-Butyldimethylsilyl (*E*)-5-phenyl-2-penten-4-ynyl ether.** *tert*-Butyldimethylsilyl (*E*)-3-iodo-2-propenyl ether (2.16 g, 0.00724 mol) was coupled with phenylacetylene (1.05 mL, 0.00956 mol) as described in the Pd/Cu-catalyzed coupling procedure above using benzene (5 mL), copper(I) iodide (0.13 g, 0.683 mmol), triphenylphosphine (0.17 g, 0.658 mmol), *n*-butylamine (2.60 mL, 0.0263 mol), bis(dibenzylideneacetone)palladium (0.08 g, 0.139 mmol) and benzene (3 mL) overnight to afford 1.58 g (80%) of the title compound as a yellow oil. IR (neat) 3056.4, 2953.8, 2851.3, 1594.9, 1492.3, 1471.8, 1441.0, 1374.4, 1256.4, 1128.3, 1071.8, 1030.8, 1005.1, 953.8, 912.8, 835.9, 774.4, 753.8, 692.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (m, 2 H), 7.27 (m, 3 H), 6.27 (dt, J = 15.7, 4.3 Hz, 1 H), 5.96 (dt, J = 15.7, 2.1

Hz, 1 H), 4.26 (dd, J = 4.3, 2.1 Hz, 2 H), 0.91 (s, 9 H), 0.08 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.46, 131.48, 128.29, 128.22, 128.03, 108.79, 89.65, 87.83, 63.01, 25.92, 18.40, 12.58.

***E*-5-Phenyl-2-penten-4-yn-1-ol.** *tert*-Butyldimethylsilyl (*E*)-5-phenyl-2-penten-4-ynyl ether (1.44 g, 0.00528 mol) and tetrabutylammonium fluoride (6.50 mL, 1 M in THF, 0.0065 mol) were stirred together in THF (6 mL) at room temperature for 2 h. After addition of ether (20 mL), the reaction mixture was twice washed with water. The organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. Purification by column chromatography (hexane, silica gel) yielded 0.63 g (75%) of the title compound as a yellow oil. IR (neat) 3353.8, 3056.4, 2912.8, 2861.5, 2205.1, 1953.8, 1635.9, 1594.9, 1487.2, 1441.0, 1369.2, 1302.6, 1215.4, 1087.2, 1025.6, 1000.0, 953.8, 753.8, 687.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (m, 2 H), 7.28 (m, 3 H), 6.33 (dt, J = 15.9, 5.2 Hz, 1 H), 5.96 (dt, J = 15.9, 1.8 Hz, 1 H), 4.24 (dd, J = 5.2, 1.8 Hz, 2 H), 1.68 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.77, 131.52, 128.31, 128.22, 123.21, 110.48, 90.14, 87.28, 63.01.

***E*-5-Phenyl-2-penten-4-yn-1-al.**[15] (*E*)-5-Phenyl-2-penten-4-yn-1-ol (0.63 g, 0.00398 mol) and pyridinium dichromate (2.30 g, 0.00611 mol) were stirred together in methylene chloride (10 mL) at room temperature for 2 h. After addition of ether (20 mL), the reaction mixture was filtered through Celite and the solvent was removed in vacuo to yield 0.52 g (84%) of the title compound as a yellow oil. IR (neat) 3056.4, 2923, 2820, 2725, 2194.9, 1682.1, 1605.1, 1487.2, 1441.0, 1394.9, 1292.3, 1117.9, 1071.8, 1035.9, 994.9, 959.0, 759.0, 687.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.60 (d, J = 7.8 Hz, 1 H), 7.49 (m, 2 H), 7.37 (m, 3 H), 6.80 (d, J = 15.9 Hz, 1 H), 6.50 (dd, J = 15.8, 7.8 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.00, 139.16, 132.44, 132.05, 129.84, 128.56, 121.78, 104.18, 86.03.

***E*-1-Phenylhexa-3-ene-1,5-diyne.**[16] Carbon tetrabromide (2.25 g, 0.00678 mol), triphenylphosphine (1.80 g, 0.00686 mol) and zinc dust (0.45 g, 0.00688 mol) were stirred together in methylene chloride (4 mL) for 24 h. Then (*E*)-5-phenyl-2-penten-4-yn-1-al (0.52 g, 0.00336 mol) was added and the mixture was stirred for 2 h. The resulting suspension was poured into hexane. The precipitated material was filtered off and redissolved in methylene chloride. Addition of more hexane precipitated the salts again. Three more cycles of dissolution, precipitation and filtration ensured complete separation of the desired product from the byproducts. The solvent from the combined hexane washes was removed in vacuo to yield the crude 1,1 dibromoalkene. This crude material was cooled in THF to -78°C and then n-butyllithium (4.50 mL, 1.49 M, 0.00671 mol) was added. The reaction mixture was stirred at -78°C for 1 h and then at room temperature for 1 h. Excess water was added to quench the reaction. After phase separation, the organic phase was twice washed with water and then dried over magnesium sulfate. The solvent was removed in vacuo and the crude product was purified by chromatography to yield 0.0958 g (19%) of the title compound as a yellow oil. IR (neat) 3292.3, 3035.9, 2194.9, 1753.8, 1600.0, 1487.2, 1441.0, 1287.2, 1071.8, 1030.8, 933.3, 753.8, 687.2 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (m, 2 H), 7.31 (m, 3 H), 6.28 (dd, J = 16.1, 0.4 Hz, 1 H), 6.02 (dd, J = 16.1, 2.4 Hz, 1 H), 3.18 (dd, J = 2.5, 0.7 Hz, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 132.04, 129.15, 128.78, 123.34, 123.03, 119.91, 95.41, 87.68, 82.71, 82.33.

Polymer of Z-1,5-dodecadiyn-3-ene. Z-1,5-Dodecadiyn-3-ene (0.94 g, 0.00587 mol) in benzene (5 mL) was heated to 120°C overnight in a screw cap tube. After cooling to room temperature, the tube was opened and the solvent was removed *in vacuo* to yield 0.78 g (82.9%) of a polymer soluble in methylene chloride and THF. IR (KBr) 2955.1, 2928.6, 2857.4, 1460.3, 1248.7, 1160.9, 1114.5, 1053.3, 839.9, 758.1, 728.3, 688.0 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.0-6.8 (m), 6.2-5.4 (m), 2.6-1.8 (m), 1.8-1.1 (m), 1.1-0.6 (m), 0.4--0.3 (m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132-124 (m), 31 (br), 28 (br), 22 (br), 14 (br). TGA (10°C/min, N_2) weight loss at 900°C 66.17%, $T_{10\%}$ 287°C, $T_{50\%}$ 472°C. GPC (THF, 60°C): M_w= 3930, M_n = 1570, M_w/M_n = 2.49. Analysis calculated for $C_{12}H_{16}$: C 89.93, H 10.07. Found C 76.54, H 8.47. This alkylated derivative had residual alkene in it which was apparent by the presence of the alkenyl protons. Aryl to alkenyl proton integration ratio was 10:1.

Polymer of Z-1-phenylhexa-3-ene-1,5-diyne. Z-1-Phenylhexa-1,5-diyn-3-ene (1.07 g, 7.03 mmol) in benzene (3 mL) was heated to 150°C overnight in a screw cap tube. After cooling to room temperature, the tube was opened and the solvent was removed *in vacuo* to yield 0.97 g (90.7%) of a polymer soluble in methylene chloride and THF. IR (KBr) 3053.2, 3023.6, 2971.8, 2926.4, 2865.4, 1596.7, 1488.9, 1440.8, 1114.0, 1069.7, 1026.6, 910.8, 838.2, 753.2, 691.4, 524.5 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.0-6.6 (m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132-126 (br m). TGA (10°C/min, N_2) weight loss at 900°C

42.41%, $T_{10\%}$ 392°C. GPC (THF, 60°C): $M_w = 305000$, $M_n = 9500$, $M_w/M_n = 32$. Analysis calculated for $C_{12}H_8$: C 94.70, H 5.30. Found C 86.96, H 5.14.

Polymer of 1,2-diethynylbenzene. 1,2-Diethynylbenzene (0.38 g, 0.00254 mol) in benzene (2.50 mL) was heated to 170°C overnight in a screw cap tube. After cooling to room temperature, a red brown solid was removed by filtration and washed with ether to yield 0.33 g (86%) of the title compound as an insoluble solid. IR (KBr) 3058.6, 1595.0, 1475.1, 1159.2, 875.1, 753.8, 644.0 cm^{-1}. Analysis calculated for $C_{10}H_6$: C 95.20%, H 4.80%. Found C 91.48%, H 4.88%. TGA (10°C/min, N_2) weight loss at 900°C 31.85%, $T_{10\%}$ 500°C. Analysis calculated for $C_{10}H_6$: C 95.20, H 4.80. Found C 91.48, H 4.88.

Polymer of 1,2-bis(2'-phenylethynyl)benzene. 1,2-Bis(2'-phenylethynyl)benzene (0.50 g, 0.00180 mol) was heated as a neat liquid to 400°C in a sealed glass tube overnight. After cooling to room temperature, the tube was opened to yield 0.33 g (66%) of a black insoluble polymer and 0.15 g (30%) of an ether soluble material which was mono or dimeric. IR (KBr) 3049.1, 2928.9, 2868.5, 1595.9, 1438.7, 1155.7, 1111.9, 1026.3, 872.4, 751.2, 697.0 cm^{-1}. TGA (10°C/min, N_2) weight loss at 900°C 17.98%, $T_{10\%}$ 606°C.

Polymer of 1,2-di(1'-octynyl)benzene. 1,2-Di(1'-octynyl)benzene (1.15 g, 0.00391 mol) was heated as a neat liquid to 340°C in a sealed glass tube overnight. After cooling to room temperature, the tube was opened to yield 0.21 g (18.5%) of a black insoluble polymer and 0.32 g (27.8%) of an ether soluble material that proved to be mono or dimeric. For the insoluble material: IR (KBr) 3040.3, 2924.5, 2859.5, 1597.5, 1583.7, 1438.5, 1376.1, 1165.0, 1119.5, 870.2, 747.9 cm^{-1}. TGA (10°C/min, N_2) weight loss at 900°C 27.68%, $T_{10\%}$ 507°C. Analysis calculated for $C_{22}H_{30}$: C 89.8%, H 10.2%. Found C 93.25%, H 4.40%.

Polymer of Z-1,6-di(trimethylsilyl)hexa-3-ene-1,5-diyne. *Z*-1,6-Di(trimethylsilyl)hexa-1,5-diyn-3-ene (1.37 g, 6.21 mmol) was heated as a neat liquid to 300°C in a sealed glass tube overnight. After cooling to room temperature, the tube was opened to yield 1.03 g (75.2%) of a polymer soluble in methylene chloride and THF. IR (KBr) sh above 3000, 2955.0, 1404.6, 1250.8, 1045.3, 838.0, 686.3 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.0-6.8 (m), 0.6-$^-$0.4 (m). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 150-118 (m), 5-$^-$3 (m). TGA (10°C/min, N_2) weight loss at 900°C 62.75%, $T_{10\%}$ 248°C, $T_{50\%}$ 490°C. GPC (THF, 60°C): $M_w = 2850$, $M_n = 1040$, $M_w/M_n = 2.74$. Analysis calculated for $C_{12}H_{20}$: C 65.38%, H 9.14%. Found C 64.83%, H 8.15%.

Polymer of Z-7,11-octadecadiyn-9-ene. *Z*-7,11-Octadecadiyn-9-ene (1.22 g, 0.00499 mol) in benzene (5 mL) was heated to 140°C overnight in a screw cap tube. After cooling to room temperature, the tube was opened to yield 1.07 g (87.7%) of an oil soluble in methylene chloride and THF. IR (KBr) 2924.8, 2858.4, 2216.1, 1676.2, 1576.5, 1460.2, 1377.2, 1327.3, 1116.9, 740.4, 718.3, 696.1 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.66 (m), 7.53-7.41 (m), 5.70 (br s, from residual starting material), 2.37 (t, J = 6.9 Hz), 1.56 (q, J = 6.9 Hz), 1.50-1.10 (br m), 0.87 (t, J = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 132, 128, 118, 97, 31, 28, 22, 19, 14. GPC (THF, 60°C): $M_w = 980$, $M_n = 810$, $M_w/M_n = 1.21$. TGA (10°C/min, N_2) weight loss at 900°C 97%, $T_{10\%}$ 178°C, $T_{50\%}$ 375°C. This data supported the fact that most of the material was unreacted starting material.

Polymer of Z-1-(2'-biphenyl)hexa-3-ene-1,5-diyne. *Z*-1-(2'-biphenyl)hexa-3-ene-1,5-diyne (2.56 g, 11.1 mmol) in benzene (10 mL) was heated to 50°C overnight in a screw cap pressure tube under nitrogen. For the next two days the reaction was then heated to 90°C. After cooling to room temperature, the solvent was removed *in vacuo* to give a yellow brown solid. This solid was dissolved in methylene chloride and then fractionally precipitated with hexane to yield 1.13 g (44%) of the title compound as a yellow brown solid. IR (KBr) 3056.4, 3025.6, 2953.8, 1594.9, 1476.9, 1430.8, 1246.2, 1159.0, 1112.8, 1071.8, 1010.3, 948.7, 912.8, 841.0, 753.8, 697.4, 615.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.8 - 6.6 (br m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 145 - 139 (br m), 134 - 132 (br), 129.1, 127.8, 121.9 (br). TGA (10°C/min, N_2) $T_{10\%}$ 432°C, $T_{50\%}$ 791°C, weight loss at 900°C 54.2%. GPC (THF, 60°C): $M_w = 3200$, $M_n = 2000$, $M_w/M_n = 1.6$. Analysis calculated for $C_{18}H_{12}$: C 94.70, H 5.30. Found C 91.66, H 5.60.

Polymer of Z-1-(4'-biphenyl)hexa-3-ene-1,5-diyne. *Z*-1-(4'-biphenyl)hexa-3-ene-1,5-diyne (0.24 g, 1.06 mmol) in benzene (1 mL) was heated to 95°C overnight in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was removed *in vacuo* to give a yellow brown solid. This solid was dissolved in methylene chloride and then fractionally precipitated with hexane to yield 0.18 g (76%) of the title compound as a yellow brown solid. IR (KBr) 3025.6, 1600.0, 1487.2, 1400.0, 1179.5, 1107.7, 1076.9, 1005.1, 835.9, 764.1, 697.4 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.0 - 6.8 (br m). ^{13}C

NMR (75 MHz, $CDCl_3$) δ 142 - 138 (br), 133 - 131 (br), 128.8, 127.0, 123 - 120 (br). TGA (10°C/min, N_2) $T_{10\%}$ 438°C, weight loss at 900°C 39.9%. GPC (THF, 60°C): M_w = 10600, M_n= 4100, M_w/M_n = 2.6. Analysis calculated for $C_{18}H_{12}$: C 94.70, H 5.30. Found C 91.98, H 5.26.

Polymer of *Z*-1-(1'-naphthyl)hexa-3-ene-1,5-diyne. *Z*-1-(1'-naphthyl)hexa-3-ene-1,5-diyne (1.45 g, 7.17 mmol) in benzene (7 mL) was heated to 115°C overnight in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was removed *in vacuo* to yield 1.34 g (92.4%) of the title compound as a yellow brown solid. IR (KBr) 3041.0, 1559.0, 1508.1, 1457.3, 1391.9, 1014.1, 905.1, 861.5, 786.2, 774.4, 730.8 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.0 - 6.8 (br m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135 - 132 (br), 131 - 123 (br), 122 - 120 (br), 122 - 120 (br), 96 - 91(br m). TGA (10°C/min, N_2) $T_{10\%}$ 428°C, weight loss at 900°C 35.2%. GPC (THF, 60°C): M_w = 5500, M_n = 1450, M_w/M_n = 3.8. Analysis calculated for $C_{16}H_{10}$: C 95.02, H 4.98. Found C 90.36, H 4.90.

Polymer of *Z*-1-[4'-(*tert*-butyl)phenyl]hexa-3-ene-1,5-diyne. *Z*-1-[4'-(*tert*-Butyl)phenyl]hexa-3-ene-1,5-diyne (0.53 g, 2.54 mmol) in benzene (1.5 mL) was heated to 50°C for 3 h in a screw cap pressure tube under nitrogen. Then the reaction was heated to 85°C for 2.5 h and to 95°C overnight. After cooling to room temperature, the solvent was removed *in vacuo* to yield 0.45 g (84%) of the title compound as a brown solid soluble in methylene chloride and THF. IR (KBr) 3025.6, 2964.1, 2902.6, 2871.8, 1507.7, 1461.5, 1394.9, 1364.1, 1266.7, 1200.0, 1107.7, 1020.5, 830.8 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.6 - 6.9 (br m), 1.5 - 0.9 (br m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153 - 147 (br), 131.6, 128.9, 125.6, 121.1, 35.1, 31.7. TGA (10°C/min, N_2) $T_{10\%}$ 428°C, weight loss at 900°C 49.2%. GPC (THF, 60°C): M_w = 6500, M_n = 2600, M_w/M_n = 2.5. Analysis calculated for $C_{16}H_{16}$: C 92.26, H 7.74. Found C 90.22, H 7.66.

Polymer of *Z*-1-(9'-anthracenyl)hexa-3-ene-1,5-diyne. *Z*-1-(9'-anthracenyl)hexa-3-ene-1,5-diyne (0.69 g, 2.73 mmol) in benzene (10 mL) was heated to 120°C overnight in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was removed *in vacuo* to give an orange solid. This solid was partially dissolved in methylene chloride. The insoluble portion was filtered off to yield 0.41 g (51%) of the title compound as an orange solid. Insoluble portion: IR (KBr) 3046.2, 2923.1, 2851.3, 1656.4, 1564.1, 1441.0, 1405.1, 1256.4, 1159.0, 1128.2, 1010.3, 948.7, 882.1, 841.0, 733.3, 610.3 cm^{-1}. Analysis calculated for $C_{20}H_{12}$: C 95.20, H 4.80. Found C 90.30, H 4.84. TGA (10°C/min, N_2) $T_{10\%}$ 351°C, weight loss at 900°C 33.4%. Soluble portion: ^1H NMR (300 MHz, $CDCl_3$) δ 8.6 – 6.9 (br m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 135 - 120 (br m), 118 - 117 (br), 68 - 66 (br m), 44 - 40 (br m), 40 - 37 (br m), 34 - 32 (br m), 30.1, 29 - 22 (br m), 14.5, 11.4, 2 - 0 (br m). GPC (THF, 60°C): M_w = 9400, M_n = 800, M_w/M_n = 11.8. The GPC trace was multimodal possibly caused by Diels-Alder reactions of the anthracene groups.

Polymer of 1-(ethynyl)-2-(2''-phenylethynyl)benzene. 1-(Ethynyl)-2-(2''-phenylethynyl)benzene (0.40 g, 2.54 mmol) in benzene (1.5 mL) was heated to 140°C overnight in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was evaporated to yield the title compound as a brown solid soluble in methylene chloride and THF. IR (KBr) 3060.4, 3026.2, 1595.8, 1493.2, 1459.0, 1438.4, 1157.8, 1068.9, 1027.8, 754.0, 699.3 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.2 – 6.4 (br m). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134 - 121 (br m). TGA (10°C/min, N_2) $T_{10\%}$ 380.70°C, $T_{50\%}$ 617.11°C, weight loss at 900°C 56.8%. GPC (THF, 60°C): M_w = 1200, M_n = 850, M_w/M_n = 1.4. Analysis calculated for $C_{16}H_{10}$: C 95.02, H 4.98. Found C 93.41, H 5.14.

Polymer of 3-(2'-phenylethynyl)-4-ethynylthiophene. 3-(2'-Phenylethynyl)-4-ethynylthiophene (0.80 g, 2.86 mmol) in benzene (3 mL) was heated to 160°C for 1 day in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was removed *in vacuo* . The resulting brown solid was dissolved in methylene chloride and then fractionally precipitated with hexane to yield 0.53 g (66%) of the title compound as a brown solid. IR (KBr) 3101.5, 3060.4, 1595.8, 1493.2, 1436.4, 1383.7, 1103.1, 1068.9, 877.2, 795.1, 754.0, 692.4 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.8 - 6.8 (br m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148 - 120 (br m), also small amounts of alkyne residues at 91.9 (br), 85.2 (br). TGA (10°C/min, N_2) $T_{10\%}$ 445.7°C, $T_{50\%}$ 747°C, weight loss at 900°C 64.1%. GPC (THF, 60°C): M_w = 3470, M_n = 1280, M_w/M_n = 2.7. Analysis calculated for $C_{14}H_8S$: C 80.73, H 3.87. Found C 79.94, H 3.89.

Polymer of 2,3-Bisethynylbenzothiophene. 2,3-Bisethynylbenzothiophene (0.86 g, 0.00472 mol) in benzene (5 mL) was heated to 150°C for 1 day in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was removed *in vacuo* to yield 0.79 g (92%) of the title compound as a brown insoluble solid. IR (KBr) 3055.6, 1580.8, 1435.5, 1312.0, 1159.4, 1130.3, 1065.0, 1021.4, 847.0, 759.8, 730.8, 679.9, 650.9 cm^{-1}. TGA (10°C/min, N_2) $T_{10\%}$ 410°C, weight loss at 900°C 30.1%. Analysis calculated for $C_{12}H_6S$: C 79.09, H 3.32. Found C 78.20, H 3.63.

Polymer of *E*-1-Phenylhexa-3-ene-1,5-diyne. *E*-1-Phenylhexa-3-ene-1,5-diyne (0.0958 g, 0.000630 mol) in benzene (1 mL) was heated to 150°C for 2 day in a screw cap pressure tube under nitrogen. After cooling to room temperature, the solvent was removed *in vacuo* . The resulting solid was fractionally precipitated with hexane to yield 0.0600 g (63%) of brown hexane insoluble material and 0.0357 g (37%) of tan hexane soluble material. The hexane soluble material only contained aliphatic material by ^{1}H NMR. Hexane insoluble material: IR (KBr): 3046.2, 3025.6, 2933, 2861, 1625.6, 1600.0, 1487.2, 1441.0, 1384.6, 1256.4, 1164.1, 1117.9, 1025.6, 948.7, 753.8, 692.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.6 - 6.4 (br m). ^{13}C NMR (75 MHz, $CDCl_3$) δ 132 (br), 129 (br), 124 (br). TGA (10°C/min, N_2) $T_{10\%}$ 369°C, weight loss at 900°C 42.7%. GPC (THF, 60°C): $M_w = 6858$, $M_n = 2908$, $M_w/M_n = 2.36$.

ACKNOWLEDGMENTS. We are grateful for support from the Office of Naval Research and the National Science Foundation (EHR-91-08772, DMR-9158315), and generous industrial contributors to the NSF Presidential Young Investigator Award (1991-96): Hercules, IBM, Ethyl, Shell, Eli Lilly, Polaroid, and Farchan Corporations. We also thank Molecular Design Ltd. for the use of their synthetic data base.

REFERENCES AND NOTES

(1) Lockhart, T. P.; Comita, P. B.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4082. Lockhart, T. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4091. Bergman, R. G. *Acc. Chem. Res.* **1973**, *6*, 25. Jones, R. R. ; Bergman, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 660.

(2) Lee, M. D.; Dunne, T. S.; Chang, C. C.; Ellestad, G. A.; Siegel, M. M.; Morton, G. O.; McGahren, W. J.; Borders, D. B. *J. Am. Chem. Soc.* **1987**, *109*, 3466. Golik, J.; Dubay, G.; Groenewold, G.; Kawaguchi, H.; Konishi, M.; Krishnan, B.; Ohkuma, H.; Saitoh, K.; Doyle, T. W. *J. Am. Chem. Soc.* **1987**, *109*, 3462. Beau, J. M.; Crevisy, C. *Tetrahedron Lett.* **1991**, *32*, 3171. Wender, P. A.; McKinney, J. A.; Mukai, C. *J. Am. Chem. Soc.* **1990**, *112*, 5369. Nicolaou, K. C.; Dai, W.-M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1387. Konig, B. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1675. Lindh, R.; Lee, T. J.; Bernhardsson, A.; Persson, B. J.; Karlström, G. *J. Am. Chem. Soc.* **1995**, *117*, 7186.

(3) (a) For the preliminary account of this work, see: John, J. A.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 5011. (b) Recently, Bergman reported a double cycloaromatization based on a conjugated dienetriyne. See: Bharucha, K. N.; Marsh, R. M.; Minto, R. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 3120. (c) Likewise, recent tandem cyclizations have been accomplished by Grissom. See: Grissom, J. W.; Calkins, T. L.; McMillen, H. A. *J. Org. Chem.* **1993**, *58*, 6556. Grissom, J. W.; Klingberg, D. *J. Org. Chem.* **1993**, *58*, 6559. (d) A similar cascade sequence to cycloaromatize a poly(arylene-ethynylene) has been developed. See: Zhou, Q.; Swager, T. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*, 193. Grubbs, R. H.; Kratz, D. *Chem. Ber.* **1993**, *126*, 149. (e) For use of enediynes in a vapor deposition process to form polymer films, see: Moore, J. A.; Lang, C.-I.; Lu, T.-M.; Yang, G.-R. *Proc. Polym. Sci. Mat. Eng.* **1995**, *72*, 437.

(4) For some reviews on polyphenylene, see: (a) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (b) Noren, G. K.; Stille, J. K. *Macromol. Rev.* **1971**, 5, 385. (c) Elsenbaumer, R. L.; Shacklette, L. W. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (d) Tourillion, G. in ref 5c. (e) Baughman, R. H.; Brédas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.

(5) For use in light emitting diodes, see: Grem, G.; Günther, L.; Ullrich, B.; Leising, G. *Adv. Mater.* **1992**, *4*, 36.

(6) (a) Sonogashira, K.; Tohda, Y.; Hagihara, N.; *Tetrahedron Lett.* **1975**, 4467. Stephans, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313. (b) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757.

(7) In most cases invoving alkyne coupling to 1,2-dibromobenzene, we could obtain higher yields using the Pd(0)-catalyzed coupling of the alkynylzinc chloride to the arylbromide. See: Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393.

(8) CAUTION: The threaded glass tubes were obtained from Ace Glass Inc., product number 8648. Though we experienced no explosions in more than 50 reaction runs studied, thermalization processes should be carried out behind protective shielding.

(9) (a) Bellamy, L. J. *The Infra-red Spectra of Complex Molecules*, Wiley: New York, 1975. (b) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic*

Frequencies of Organic Molecules, Academic: New York 1991. (c) Mayer, R.; Kleinert, H.; Richter, S.; Gewald, K. *Angew. Chem., Internat. Ed. Engl.* **1962**, *1*, 115. (d) *The Aldrich Library of FT-IR Spectra, Edition I,* Pouchert, C. J., Ed., Aldrich Chemical Company: Milwaukee, 1985.

(10) Grissom, J. W.; Huang, D. *Angew. Chem., Internat. Ed. Engl.* **1995**, *34*, 2037.

(11) Kende, A. S.; Smith, C. A. *Tetrahedron Lett.* **1988**, *29*, 4217.

(12) Winn, L. S., Vollhardt, K. P. C. *Tetrahedron Lett.* **1985**, *26*, 709.

(13) Ried, W.; Bender, H. *Chem. Ber.* **1955**, *88*, 34.

(14) Jung, M. E., Light, L. A. *Tetrahedron Lett.* **1982**, *23*, 3851.

(15) Corey, E. J., Schmidt, G. *Tetrahedron Lett.* **1979**, 399.

(16) Corey, E. J., Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769.

(*Received* 4 *April* 1997; *revised* 9 *June* 1997; *accepted* 15 *July* 1997)